بسم الله الرحمن الرحيم

وزارة التعليم العالي

جامعة أم القرى

كلية العلوم التطبيقية

نموذج رقم (٨)

إجازة أطروحة علمية في صيغتها النهائية بعد إجراء التعديلات

الاسم (رباعي): ليلى سعيد عبد الرحيم الحرازي كلية: العلوم التطبيقية قسم: الكيمياء

الأطروحة مقدمة لنيل درجة: الماجستير في تخصص: الكيمياء الفيزيائية

عنوان الأطروحة: ((ثبات وتكسير بعض الأوبالات))

الحمد لله رب العالمين والصلاة والسلام على أشرف الأنبياء والمرسلين وعلى آله وصحبه أجمعين وبعد:

فبناءً على توصية اللجنة المكونة لمناقشة الأطروحة المذكورة أعلاه والتي تمت مناقشتها بتاريخ ١٤٢١/١٠/٢٠هـ بقبولها بعد إجراء التعديلات المطلوبة، وحيث قد تم عمل اللازم؛ فإن اللجنة توصي بإجازتها في صيغتها النهائية المرفقة للدرجة العلمية المذكورة أعلاه ...

والله الموفق ...

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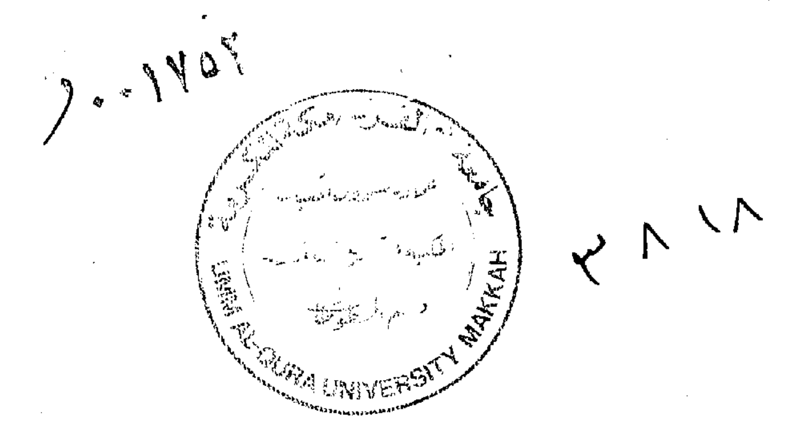
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• يوضع هذا النموذج أمام الصفحة المقابلة لصفحة عنوان الأطروحة في كل نسخة من الرسالة.

جامعة أم القرى
كلية العلوم التطبيقية
قسم الكيمياء



ثباتية و تكسير بعض الكوبلمرات

رسالة مقدمة من

ليلى سعيد المزروعي
بكالوريوس في الكيمياء

وذلك كجزء من المتطلبات للحصول على درجة الماجستير في الكيمياء

الإشراف

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١٤٢١هـ

الملخص العربي

شغلت الثباتية الحرارية للبوليمرات اهتماما كبيرا لسنوات عديدة. إن إحدى الوسائل للحصول على بوليمرات لها ثباتية حرارية هي عن طريق البلمرة المزدوجة (كوبلمرة) للمونمر الأساسي في وجود مونمر آخر.

تتضمن الرسالة تحضير بولي(فينيل أكريلاميد) وبولي (بيتا-توليل أكريلاميد) و كوبوليمرات فينيل أكريلاميد و بيتا-توليل أكريلاميد مع الميثيل ميثاأكريلات و الميثيل أكريلات بهدف دراسة الثبات الحراري و نواتج التكسير الحراري للبوليمرات المتكونة و قياس طاقة التنشيط للتكسير الحراري.

و تشتمل الرسالة على خمسة أبواب، يحتوي الباب الأول على استعراض للبحوث المنشورة عن ميكانيكية الثبات و التكسير الحراري للبوليمرات المختلفة.

و يتضمن الباب الثاني طرق تحضير المونمرات و البوليمرات محل الدراسة و طرق التحليل المختلفة المستخدمة لدراسة الثباتية و التكسير الحراري للبوليمرات.

و تشتمل الأبواب الثالث و الرابع و الخامس النتائج المستخلصة من هذه الدراسة. فيتضمن الباب الثالث دراسة الثبات الحراري لهوموبوليمرات الفينيل أكريلاميد و خمس تركيبات مختلفة التركيز من كوبوليمرات الفينيل أكريلاميد مع الميثيل ميثاأكريلات، حيث أمكن تعيين نسبة النشاطية للمونمرات في الكوبوليمرات باستخدام طيف الرنين النووي المغناطيسي. أثبت التحليل الحراري أن كوبوليمرات الفينيل أكريلاميد مع الميثيل ميثاأكريلات لها ثباتية حرارية محصورة بين هوموبوليمرات الفينيل أكريلاميد و الميثيل ميثاأكريلات. عند دراسة نواتج التكسير الحراري لهوموبوليمرات الفينيل أكريلاميد باستخدام الكروماتوجراف الغازي المتصل بمطياف الكتلة، يتضح أن ميكانيكية تكسير الهوموبوليمرات عبارة عن تكسير في روابط كربون-نيتروجين لتكوين شقوق طليقة. اتحاد هذه الشقوق مع بعضها أو التكسير العشوائي لها من خلال السلسلة الأساسية يكون مصدر النواتج العديدة لتكسير الهوموبوليمر. كذلك تم دراسة نواتج التكسير الحراري لكوبوليمرات فينيل أكريلاميد مع الميثيل ميثاأكريلات، ووجد أنها نفس نواتج التكسير الحراري لهوموبوليمرات الفينيل أكريلاميد و الميثيل ميثاأكريلات.

و يتضمن الباب الرابع تحضير هوموبوليمرات بيتا-توليل أكريلاميد و خمسة تركيزات مختلفة من كوبوليمرات بيتا-توليل أكريلاميد مع الميثيل ميثاأكريلات، ووجد أن نسبة النشاطية في الكوبوليمر ١,٤ ± ٠,١ & ٢,٧ ± ٠,١ على التوالي. أثبت التحليل الحراري الوزني أن ثباتية

الكوبوليمرات تقع بين هوموبوليمرات بيتا-توليل أكريلاميد و الميثيل ميثاأكريلات. كذلك تم تعيين طاقة التنشيط ووجد أنها تزداد في نفس اتجاه الثباتية الحرارية. و بدراسة نواتج التكسير الحراري للهوموبوليمر باستخدام الكروماتوجراف الغازي المتصل بمطياف الكتلة، وجد أن التكسير الحراري يتم من خلال روابط كربون-نيتروجين و كربون-كربون المتصلة بمجموعة الكربونيل لتكوين شقوق طليقة سرعان ما يتحد بعضها البعض مكونة نواتج عديدة. كذلك بدراسة نواتج التكسير الحراري لكوبوليمرات بيتا-توليل أكريلاميد و الميثيل ميثاأكريلات لم تتكون مركبات جديدة خلاف ما تم الحصول علية من هوموبوليمرات بيتا-توليل أكريلاميد و الميثيل ميثاأكريلات.

و أخيراً فيشمل الباب الخامس على تحضير خمس تركيزات مختلفة من كوبوليمرات بيتا-توليل أكريلاميد مع الميثيل أكريلات و تعيين نسبة النشاطية للمونومرات المستخدمة في عملية البلمرة ووجد أنها تساوي ٠,٥٨ ± ٠,١ & ١,٥٢ ± ٠,١ على التوالي. ووجد أن ثباتية الكوبوليمرات تزداد بزيادة تركيز الميثيل أكريلات في الكوبوليمرات. و بدراسة نواتج التكسير الحراري للكوبوليمرات ، وجد ثاني أكسيد الكربون و الكحول الميثيلي و مركبات كربونية مختلفة و هي نفس نواتج التكسير الحراري لبولي ميثيل أكريلات و كذلك نفس نواتج التكسير الحراري لبولي بيتا-توليل أكريلاميد. كذلك تم قياس طاقة تنشيط التكسير الحراري للكوبوليمرات، ووجد أنها بين ١١٣,٣-١٣٨,٥ كيلو جول/مول، و تزداد قيمتها بزيادة تركيز الميثيل أكريلات في الكوبوليمر.

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STABILITY AND DEGRADATION OF SOME NEW COPOLYMERS

By
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B.Sc. in Chemistry

A Thesis
Submitted in Partial Fulfillment of the Requirements for the Master Degree in Chemistry
(M.Sc.)

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قال تعالى[1]:

﴿ وقل ربي زدني علماً ﴾

TO MY DEAR
MOTHER

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ACKNOWLEDGMENT

Thanks to Allah the Almighty for his bless with me and helping during all stages of my life.

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INTRODUCTION

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INTRODUCTION

The degradation of polymers under normal use conditions is a major factor limiting application of these remarkable and versatile materials. Without exception, all polymers are degraded eventually within the environment to which they are exposed during their life cycle. Though there is considerable variation between polymers in their resistance to degradation, eventually important properties of every polymer are affected adversely as those chemical reactions responsible for degradation proceed. Loss in mechanical strength, dielectric quality and aesthetic appearance often lead to failure of polymeric materials before reaching the required service life[1].

Stabilization is required to extend the useful life of most polymers. Compounding with selected additives (stabilizers) is the favored method for improving stability. Alteration of polymer molecules to provide more resistant structures has a limited role in stabilization. In altering the structure of a polymer to obtain a required level of stability, every other important property of that polymer must be held within specified limits. This is difficult at best and usually impossible to accomplish.

Development of the art of stabilization into a science took place rapidly after Hoffman reported[2] in 1861 that degradation of natural rubber was accompanied by absorption of oxygen. Inhibition of the degradation process by addition of phenols or amines was observed by many of the earlier investigators[3-5]. Over the course of several decades, it was finally established that the degradation of natural rubber occurred by a free-radical initiated[6], chain mechanism[7-9]. The misleading hypothesis that stabilizers functioned as oxygen scavengers was abandoned as it was recognized that protection was provided by those additives which in some way inhibited one or more of the reactions occurring in the polymer. The term "anti-ger" or "anti-oxygen" was then abandoned in favor of the modern term "antioxidant " to describe the class of

stabilizers which protects against oxygen-induced degradation. As the science of stabilization developed, several other types of stabilizers appeared, each functioning at a specific stage in the degradation mechanism. Stabilizers were developed to protect against ultraviolet – induced degradation, ozone attack, and ionizing radiation.

The key point which evolved from the early history of polymer stabilization was simply that a scientific approach could only be developed after the mechanism responsible for degradation had been established. Because of the complexity of polymer reactions, much of the early mechanistic studies were developed through the use of model compounds. Despite the obvious fact that a perfect model for a complex polymer molecule is difficult to devise, experiments with simple compounds made an invaluable contribution to elucidation of degradation mechanisms for several polymers. Studies on the oxidation of hydrocarbons at the Natural Rubber Producers Research Association[10,11] provided the basic understanding for the degradation of natural rubber as well as the polyolefins.

Polymers degrade by several different mechanisms, depending on structure and exposure conditions. Degradation results from an irreversible change, which leads eventually to failure. The most common types of degradation occur through chemical reactions, but there are a few important examples of degradation resulting only from physical changes. This latter type of degradation results from disruption of polymer morphology, rather than reactions at the molecular level. The phenomena of environmental stress cracking[12] and thermal embrittlement[13] are examples of physical degradation. Though not studied as extensively as chemical degradation, when these changes do occur, they can result in rapid and complete failure.

Studies of degradation which takes place during exposure to heat in the total absence of oxygen require very sophisticated experimental techniques. High vacuum technology has been used by many investigators in the study of

thermal degradation or pyrolysis. This research has been important in determining the relative strength of bonds in polymer molecules. As energy is absorbed and distributed through the molecules, a point is reached at which the energy concentrated at one bond in the molecule exceeds its dissociation energy. When this point is reached, the bond ruptures and unless it can reform, an irreversible chemical change will take place.

By rigid definition, pyrolysis of a polymer is thermal degradation in the complete absence of any external reactant. Thermal degradation, however, usually results from the combined effects of pyrolysis and thermal oxidation. The earliest experiment on record of thermal degradation in an atmosphere of limited oxygen content is credited to Williams[14] who in 1860 demonstrated that isoprene is formed when natural rubber is heated. There then followed a long sequence of research papers[15,16] dealing with the pyrolysis of natural rubber and synthetic polymers.

It is known that, polymers pyrolyze by one of three mechanisms or by combination of two or more of these mechanisms. Random scission, which is the predominant reaction in polyolefins, occurs through scission of bonds along the backbone chain. As the term implies, scission is a random event, and polymer molecules are first broken into large macroradicals. There is a rapid decrease in molecular weight and almost no monomer is formed in the early stages.

Depolymerization is the second general mechanism of pyrolysis. This reaction is usually initiated at chain ends. Monomer units are split off sequentially. Since only a small fraction of the molecules react at the beginning, there is very little change in molecular weight. Once depolymerization has been initiated in a molecule, the reaction proceeds until that molecule has depolymerized completely. Polyacetals and poly(methyl methacrylate) pyrolyze by depolymerization.

Poly(vinyl chloride) (PVC) pyrolyzes by the third general mechanism. This mechanism is characterized by the elimination of a low-molecular-weight fragment-other than monomer. The splitting off of hydrogen chloride from PVC leads to discoloration[17,18]. Chlorine atoms at defected points of PVC could be sites for initiation of dehydrochlorination. Catalyst residues at chain ends may also contribute to initiation. There is an evidence[19] indicating that normal groups in the backbone chain could also be involved under certain reaction conditions. The importance of defect structures on initiation PVC dehydrochlorination has been confirmed by Starnes and coworker[20] who have succeeded in replacing labile chlorine atoms with stable ligands by the following reaction:

$$\sim\sim CH_2 - \underset{\displaystyle H}{\overset{\displaystyle Cl}{\overset{|}{\underset{|}{C}}}} - CH - CH \sim\sim \quad + \quad \underset{(MLCl)}{ML_2} \longrightarrow$$

$$\sim\sim CH_2 - \overset{\displaystyle L}{\overset{|}{CH}} - CH - CH \sim\sim \quad + \quad \begin{matrix} MLCl \\ MLCl_2 \end{matrix}$$

in which M is Ba, Cd, Zn, Ca or Pb and the ligand, L, is $- O_2 CR - OR$, - SR, etc.

Poly (methyl methacrylate) (PMMA) is a clear, transparent polymer often used as a glazing material. However, this polymer depolymerizes almost completely when heated above 300 °C. A similar polymer, poly(methyl acrylate) (PMA) is more resistant to depolymerization. Copolymers of methyl methacrylate and methyl acrylate have been prepared as possible replacements for PMMA. These copolymers would be expected to be more resistant to depolymerization than the homoplymer. The anticipated improvement in stability was realized, but the copolymers did not have properties making them suitable as replacements for PMMA[19].

The thermal degradation of polystyrene (PS) has received a great deal of attention, and yet the mechanism of degradation is still the subject of controversy. However, the nature of the volatile products has led to general agreement on a number of points. The mechanism of degradation usually proposed involves both intra-and intermolecular transfer[21-24], but the ways in which these various reactions are initiated has, as yet, not been resolved completely. The thermal degradation of polystyrene starts at ~ 300°C and the products typically contain monomer comprising 42% of the original sample mass, with progressively decreasing amounts of dimer, trimer, tetramer, pentamer and small amounts of toluene and benzene.

Polyoxymethylene (POM), a polymer of formaldehyde, belongs to the generic class of polyethers or acetal resins. Its rapid depolymerization in the absence of oxygen limited the development of this polymer for many years. Formaldehyde reacts spontaneously to form low-molecular-weight oligomers which rapidly revert back to monomer. Reaction is initiated at chain ends and depolymerization then proceeds sequentially along the backbone chain. Stable polymer of formaldehyde were not known until MacDonald[25] developed a process for endcapping the macromolecules through acetylation of the terminal hydroxyl groups.

$$\sim\!\sim CH_2-O-CH_2-O-CH_2-OH \;+\; (CH_3CO_2)_2O \longrightarrow \sim\!\sim CH_2-O-CH_2-O-CH_2-OCOCH_3$$

This and similar reactions have made possible the polymerization of formaldehyde into high-molecular-weight polymers having considerable commercial importance. However, end-capped POM is still valunerable to random cleavage along the backbone chain. This reaction would then be followed by depolymerization proceeding toward the original chain ends.

$$\sim\!\sim CH_2-O-CH_2-O-(CH_2-O)_n-CH_2-OCOCH_3 \longrightarrow$$

$$\sim\!\sim CH_2-\dot{O} + \dot{C}H_2-O-(CH_2-O)_n-CH_2-OCOCH_3 \longrightarrow n+1\ CH_2O$$

Although some studies[26] have shown that commercial POM contains both aldehydic and α,β-unsaturated carbonyl groups.

Thermal degradation of polypropylene (PP) occurs primarily by random scission along the backbone chain with formation of large radical fragments as the initial step and with little or no initial weight loss. Subsequent reactions of intramolecular chain transfer then take place leading to the formation of many, low-molecular-weight hydrocarbon products[27]. This mechanism is in contrast to the elimination mechanisms in which either substituent groups are split off as in PVC or monomer units are eliminated sequentially as in POM. Random chain scission is the dominant mechanism in the pyrolysis of polyolefins and most vinyl polymers.

Many polymers degrade thermally by combinations of the basic mechanisms. Polystyrene, for example, degrades by random chain scission in the temperature range 280 – 360°C with negligible formation of volatiles[28]. At higher temperatures, however, elimination reactions take place at a significant rate with yields of the monomer as high as 40 weight percent observed at elevated temperatures[29]. PP degrades by both scission and elimination mechanisms, but its pyrolysis in the absence of oxygen yields much smaller amounts of monomer, chain scission being the dominant reaction even at elevated temperatures.

Most of the early studies[27,30] on the pyrolysis of PP were conducted under high vacuum. Chien and coworkers[31,32] in 1980 have investigated the thermal degradation of this polymer in a stream of inert gas, e.g. helium. When primary products of decomposition are swept out of the reaction zone, secondary reactions are minimized. This latter technique is considered to be

more realistic in studying the burning of polymers in which pyrolysis within the polymer bulk is the initial step, and volatiles are swept away from the area where pyrolysis is taking place. Of course, different secondary reactions occur in the flame zone above the burning polymer.

There are differences, largely quantitative, between the products formed during the thermal degradation of PP in vacuum and in an inert gas stream. However, reactions leading to the products are similar and follow the mechanism under helium as proposed by Chien[31,32].

$$\sim CH_2-CH(CH_3)-CH_2-CH(CH_3)-CH_2-CH(CH_3)-CH_2-CH(CH_3)\sim \longrightarrow$$

$$\sim CH_2-CH(CH_3)-CH_2-\dot{C}H(CH_3) \quad + \quad \dot{C}H_2-CH(CH_3)-CH_2-CH(CH_3)\sim$$

I

Weak links are believed to be primary sites for initiation. The secondary radical (I) then undergoes intramolecular chain transfer reactions as follow:

$$CH_3-CH(-CH_2-\dot{C}H-CH_3)-CH_2-CH(CH_3)-CH_2 \,|\, CH(CH_3)-CH_2-CH(CH_3)\sim \longrightarrow$$

$$CH_3-CH(-CH_2-CH_2-CH_3)-CH_2-C(CH_3)=CH_2 \quad + \quad \cdot CH(CH_3)-CH_2-CH(CH_3)\sim$$

Formation of saturated hydrocarbons:

$$\sim CH(CH_3)-CH_2-CH(CH_3)-CH_2 \,|\, CH(CH_3)-CH_3 \longrightarrow$$

$$\sim CH(CH_3)-CH_2-CH(CH_3)-\dot{C}H_2 \; + \; \cdot CH(CH_3)-CH_3$$

This scission at the chain end is then followed by hydrogen abstraction to form propane and other polypropylene radical (II).

$$\underset{(PP)}{\sim CH(CH_3)-CH_2-CH(CH_3)-CH_2\sim} \; + \; \cdot CH(CH_3)-CH_3 \longrightarrow HCH(CH_3)-CH_3 \; + \; \underset{II}{PP^{\cdot}}$$

Other saturated products are presumed to be formed by a depolymerization mechanism:

$$\sim CH_2-CH(CH_3)-CH_2-\dot{C}H(CH_3) \longrightarrow \sim CH_2-\dot{C}H(CH_3) \; + \; CH_2{=}CH(CH_3)$$

Though not as firmly established, similar reactions are believed to take place in other polymers which degrade by chain scission. In all of these reactions, volatiles accumulate slowly via a series of secondary reactions following the initial chain scission. Those polymers which pyrolyze primarily by elimination mechanisms, on the other hand, yield large volumes of volatile in the initial stage of degradation. Since only a few molecules react initially, there is little change in the molecular weight of the sample until reaction has proceeded extensively.

The use of copolymers and polymer blends is increasing rapidly as various applications require properties not found in single polymers. Thermal degradation of these materials presents some unique features in addition to the basic mechanisms discussed so far. Impact modified polymers and heat-resistant copolymers are typical examples. Many important examples of both blends and copolymers have been studied by Grassie[33-35] and McNeill[36-38].

The blend of polystyrene and polyisoprene is an example of an impact-modified polymer. In the pyrolysis of this blend[39], each component degrades in a manner different from that observed when polyisoprene is degraded separately. Thermal gravimetric analysis shows that both the rate of volatile formation and the rate of chain scission of polyisoprene are reduced when blended with polystyrene, but products of the pyrolysis are essentially identical, qualitatively and quantitatively. Likewise, polystyrene appears to be stablized against thermal degradation at 340°C when blended with polyisoprene although its chain scission appears to be accelerated at 292°C. These data can be explained by assuming that polyisoprene generates small radicals as it undergoes chain scission in the first stage of degradation. As these radicals diffuse into the polystyrene phase, hydrogen abstraction takes place, and the radicals which would normally contribute to degradation of the polyisoprene are thus stabilized. Subsequently, polystyrene chains undergo scission at sites adjacent to the radical centers. The resulting polystyrene radicals decompose only slowly below 300°C. Above this temperature, there is an apparent inhibition of its depolymerization by dipentene formed from the degrading polyisoprene. This inhibition could occur through hydrogen abstraction by polystyrene radicals from the dipentene or by coupling of the macroradicals with allylic radicals.

Poly(methyl methacrylate) (PMMA) depolymerizes almost completely when heated in the absence of oxygen. Commercial applications of PMMA may require improved heat resistance and one route to achieve this is through copolymerization. The thermal degradation of copolymers of methyl

methacrylate and maleic anhydride have been investigated by Grassie and Davidson[40]. The presence of the comonomer inhibits depolymerization of PMMA. The effect is explained on the basis that depolymerization of PMMA is initiated at unsaturated end groups. Weak links have also been proposed as Initiation sites. Thermogravimetric analysis suggests that although maleic anhydride accelerates the chain scission of PMMA, depolymerization is inhibited. As depolymerization proceeds from the point of chain scission, monomer units of methyl methacrylate split off until the first maleic anhydride unit is reached. Depolymerization stops at this point.

In recent years the flammability properties of materials, especially synthetic organic polymers, have became a major topic of research in the commercial and academic fields with the aim of producing materials which retard the burning process[41,42]. The chemistry of fire retardant centers around six elements, namely, phosphorous, antimony, chlorine, bromine, boron and nitrogen. There are various general mechanisms of fire retardant in polymeric materials[43,44]. Perhaps the most important mechanism is the degradation and decomposition reaction which may be modified to produce non-flammable volatile, usually halogenated species. On this basis, Diab was focussed upon the monomer, vinyl bromide. The products and mechanism of thermal degradation of its homopolymer and of copolymers with methyl acrylate[45], methyl vinyl ketone[46], vinyl acetate[47] and a blend of its homopolymer with poly(methyl acrylate)[48] were described. The degradation of ploy(vinyl bromide) (PVB) results in the evolution of large quantities of hydrogen bromide. This conclusion is based on the observation that the loss of one molecule of hydrogen bromide is followed by the loss of another molecule in an adjacent group until a polyene is formed. Methyl bromide was formed in the thermal degradation of copolymer of vinyl bromide with methyl acrylate according to the following mechanism[45]:

Also, methyl bromide was formed in the thermal degradation of copolymer of vinyl bromide with methyl methacrylate. Zutty and Walch[49] suggested the mechanism as follow:

The degradation behaviour of poly(β-bromostyrene) homopolymer, β-bromostyrene–methyl methacrylate and β-bromostyrene–methyl acrylate copolymers were investigated, respectively[50,51]. The reactivity ratios of the copolymers were determined using NMR method. The introduction of either methyl methacrylate or methyl acrylate units into the β-bromostyrene chain leads to an interaction between the comonomer units to form compounds such as methyl bromide and anhydride structures, which are not formed in the degradation of either the homopolymers.

One of the outstanding features of the thermal degradation of polyacrylonitrile is the sudden and intense liberation of heat which occurs at approximately 265°C and which is associated with oligomerization of the nitrile groups giving a conjugated polyimine[52, 53].

The introduction of comonomers into the polyacrylonitrile molecules can have a variety of effects. Acids and amides, like acrylic acid and acrylamide, act as initiators. Another group of comonomers, which includes methyl acrylate and methyl vinyl ketone participates in the oligomerisation process. Styrene-type monomers block the reaction and suppress the exotherm. Perhaps the most promising comonomers from the point of view of carbon fibre production are certain chlorine containing comonomers which decrease the intensity of the exotherm by broadening it out over a wider temperature range without inhibiting the total reaction[54-56].

The products of thermal degradation of poly(acryloyl chloride) (PAC) homopolymer and copolymers of acryloyl chloride with methyl methacrylate (AC–MMA) have been analyzed quantitatively using thermal analysis, i.r. spectroscopy and gas–liquid chromatography[57]. The major products of degradation of PAC are HCl, CO and chain fragments. Methyl chloride, MMA monomer, CO and chain fragments are the principal products of degradation of AC–MMA copolymers.

The thermal degradation of poly(4-vinylpyridine) (PVP) and copolymers of 4-vinylpyridine and methyl methacrylate (VP-MMA) have been investigated by Diab et al[58]. The reactivity ratios of the copolymerization were determined using NMR method. The products of degradation of PVP were analyzed using

GLC and consists mainly of VP monomer and traces of pyridine and 4-methylpyridine. The degradation products of the VP-MMA copolymers are the monomers. The activation energies of the degradation of the homoplymers and copolymers were calculated.

Theoretical investigations of the products of thermal degradation of polystyrene and poly (4-vinylpyridine) have been rationalized using ASED–MO theory[59]. The calculations explain the formation of styrene dimer and the absence of 4- vinylpyridine dimer during the thermal degradation, which may be due to the high reactivity of 4- vinylpridine dimer. According to forntier molecular orbital (FMO) treatment, the reactivity of the molecule is controlled by the energy separation between HOMO and LUMO. It was found that 4-vinylpyridine dimer is more reactive than the styrene dimer due its smaller energy separation.

The oxidative degradation of polymers is a general phenomenon studied by many investigators over several decades. Failure of polymers by this mechanism is of considerable commercial importance. Without exception, all commercially- important polymers undergo reaction with oxygen, leading eventually to changes in molecular structure[60] or in morphology[61]. As a result of these reactions, critical mechanical or dielectric properties may change beyond acceptable limits. Oxidative degradation can occur during the synthesis of highly sensitive polymers. Once removed from the synthetic environment, sensitive polymers oxidize slowly even at ambient temperatures, unless adequately protected. All polymers are vuluerable oxidation during thermoforming. The environment within an extruder or an injection molding machine contains sufficient oxygen to initiate degradation. Since fabrication is usually carried out well above the polymer' s T_m, initiation sites for future oxidation are likely to be formed. Even in those processes which essentially exclude oxygen enough of the reactant is brought in with the polymer to initiate oxidation. Recognition of the potential for degradation in these early stages has lead to development of special stabilizers designed to protect during

thermoforming. Every exposure to heat, as a polymer is compounded or pellitized, presents ample opportunity for incipient oxidation to occur. Once the polymer has been fabricated into a finished product, oxidation will be proceed, though more slowly, throughout the service life. Failure is inevitable when the polymer is exposed for a long enough period. When long service life is required, almost every commercial polymer must be stabilized to inhibit oxidative degradation. Recently, attention has been directed to the importance of protecting polymer scrap which is to be recycled. Unless more protection was provided than needed for the original application, oxidation could damage the scrap as it is exposed to additional heat treatment during recycling. Most of the oxidative degradation of a polymer occurs during long-term aging, and a different type of stabilizer is required to protect the material under these conditions. There is perhaps a connection between the sites of incipient oxidation and the weak links which are believed to initiate thermal degradation in the absence of oxygen. Oxidation proceeds under service conditions as the polymer absorbs energy from one or more sources. Thermal and radiation energy (ultraviolet and high-energy radiation) are the major factors responsible for accelerating oxidative degradation, but mechanical energy can also contribute to these reactions. Each of the major energy sources promotes oxidation by a somewhat different mechanism, and appropriate stabilizers must be used for each exposure condition. Frequently, a combination of energy sources is involved in the degradation of a polymer.

The combination of oxygen as the reactant and heat as the energy source is a major factor in polymer degradation[62]. Even the most inherently-stable polymer succumb to this combination when exposed to sufficiently high temperatures for long periods. It is not surprising therefore that thermal oxidation of polymers has been studied so extensively. Emphasis has been placed on mild conditions of thermal exposure, usually referred to as autoxdation, the oxidation which occurs between ambient temperature and about 200°C. The autoxidation of hydrocarbon polymers is now well understood as a result of the extensive research conducted at the Natural

Rubber Producer' s Research Association[63, 64]. Based on this early research on model compounds for rubber, Shelton[65] has proposed the following kinetic scheme for the autoxidation of hydrocarbon polymers,

Initiation:

$$ROOH \longrightarrow RO^{\cdot} + HO^{\cdot}$$

or

$$2ROOH \longrightarrow RO^{\cdot} + ROO^{\cdot} + H_2O$$

Propagation:

$$ROO^{\cdot} + RH \longrightarrow ROOH + R^{\cdot}$$

$$R^{\cdot} + O_2 \longrightarrow ROO^{\cdot}$$

Oxidative chain branching:

$$ROOH \longrightarrow RO^{\cdot} + HO^{\cdot}$$

$$RO^{\cdot} + RH \longrightarrow ROH + R^{\cdot}$$

Eventually autotermination would take place either by coupling or disproportionation of propagating radicals, but from the practical point of view, the induced terminating reactions of stabilization are of much greater, commercial importance. In this reaction scheme, RH could represent either a low-molecular- weight hydrocarbon or a hydrocarbon polymer.

The chemical structure of hydrocarbons and hydrocarbon polymers plays an important role in autoxidation. This is evident in differences observed in the rates of oxidation of linear polyethylene, branched polyethylene and polypropylene. The bond between carbon and the hydrogens at these branced points has a law dissociation energy than that between hydrogens and carbons in the methylene group along the chain. These labile hydrogens are likely points for initiation of autoxidation and as a result branced polyethylene is measurably less stable to oxidation than the linear modification. Polypropylene, with a

methyl branch at every other carbon along the backbone chain, is less stable to autoxidation than either of the polyethylene[66].

Although polystyrene has a labile hydrogen at alternating carbons along the backbone chain, it is quite stable to autoxidation. It has been suggested[67] that stability of this polymer results either from steric protection of the labile hydrogens by the bulky aromatic rings, or from the loss of resonance energy caused by unfavorable orientation of phenyl groups in the structure[68]. In general, however, whenever branched groups are present which lower the dissociation energy of carbon hydrogen bonds, the polymer will have poor resistance to autoxidation.

Cross-linking of low-density polyethylene with peroxy carboranes was studied recently by Yuvchenko et al[69]. The stability of cross- linked polyethylene samples to oxidative thermal degradation was studied by differential thermal and thermogravimetric analyses.

Resistance of diethylene glycol esters of rosin- terpenemaleic resins to oxidative thermal degradation was studied[70]. Linear correlations were found between the temperature on the onset of oxidative thermal degradation, viscosity, and softening points of the esters.

Physical factors can also affect autoxidation rates. For example, certain semi-crystalline polymers, polyethylene being a classical example, have a crystalline structure so compact that oxygen cannot penetrate into crystallites. Oxidation of such polymers is restricted to the disordered or amorphous regions, except for slow, surface reaction of crytallites[71].

Ultraviolet radiation is responsible for the photodegradation of polymers. As in thermal oxidation, however, significant differences exist among polymers in their resistance to photooxidation. Polytetrafluoroethylene, poly(methyl methacrylate) and the urea-formaldehyde resins have exceptional stability.

Most other polymers have only moderate to poor resistance to light-induced oxidation. The polyolefins, polystyrene, poly(vinyl chloride), polyacetals, polyisoprene, and polyacrylonitrile are among the more light-sensitive polymers. In contrast to thermal oxidation, which can occur in subsurface regions of permeable polymers, photooxidation is limted to reactions at or near the polymer surface[72]. It is generally accepted that reactions involved in photooxidation are similar to those of thermal oxidation. Both are now belived to proceed by a free-radical, chain mechanism, but there are important differences between them. For instance, the length of oxidative chains in the propagation phase is much shorter than in thermal oxidation and initiation reactions are more complex. Also, photooxidation is primarily a surface reaction, suggesting that the effect of ultraviolet radiation may not extend into the polymer bulk to a significant extent. Permeation of oxygen into the polymer bulk could also strict photooxidation. Some uncertainty still persists over the initiation reactions in photooxidation to surface layers. This is not surprising since it is extremely difficult to precisely identify the very first reaction products or those sites in polymer molecules where initial reactions occur. As in thermal oxidation, it has been necessary to use model compounds in order to investigate individual chemical groupings believed to exist in complex polymer molecules. Small molecules can also be purified much more completely than polymers, thus eliminating side reactions. Early investigators were puzzled by the photooxidation of the polyolefins as contrasted to the stability of simple paraffins. If polyethylene consisted only of a carbon-carbon backbone chain with nothing but hydrogen atoms as its substituents, this polymer should have negligible absorption in the uv region, and should be as photo- stable as the simple paraffins. Double bond structures are usually responsible for absorption of uv radiation, and polymers invariably contain such groups. The presence of carbonyl groups in polyethylene was suggested by Pross and Black[73] in 1950, and Burgess[74] proposed a mechanism for photooxidation based an ketone scission reactions which are termed Norrish type I and type II reactions.

Norrish type I:

$$\sim CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_2\sim \xrightarrow{h\nu} \sim CH_2-CH_2-\overset{O}{\overset{\|}{C}}\cdot + \cdot CH_2-CH_2\sim$$

$$\sim CH_2-CH_2-\overset{O}{\overset{\|}{C}}\cdot \longrightarrow \sim CH_2-\dot{C}H_2 + CO$$

Norrish type II:

$$\sim CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-CH_2\sim \xrightarrow{h\nu} \sim CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 + CH_2=CH-CH_2\sim$$

In those structures where a hydrogen is present at the gamma carbon, quantum yield studies indicate that the type II reaction is fovored[75]. Though both reactions result in chain scission, it is important to note that only the type I reaction yields free radicals. This mechanism suggests[76] that in the photooxidation of polyethylene, carbonyl groups are the major sites of reaction as well as the groups primarily responsible for absorption of uv radiation.

Carlson and Wiles[77] in their studies of polypropylene photooxidation have emphasized the important role played by hydroperoxides. Initially, these reactive intermediates were thought to play only a minor role in the photooxdation of polyolefins since they are present in only small amounts and appreciable concentrations are detected until the reaction is well underway. However, hydroperoxides also absorb uv radiation and decomposition of these intermediates into radicals must be taken into account.

Guillet[78] in reviewing the data responsible for conflicting theories on the photooxidation of polyolefins concluded that degradation is initiated by free radicals, formed after absorption of a quantum of uv energy, either by hydroperoxides or carbonyl groups initially present. Reaction then continues by a radical-initiated, chain mechanism. Careful analysis of all available data indicates that radicals formed by the photolytic decomposition of hydroperoxides are the propagating species in photooxidation. This would account for the small amounts of hydroperoxides found in oxidizing polyolefins, and is an accord with the recognized rapid photolysis of these reactive intermediates.

Although details of this mechanism have not as yet been completely supported by experimental evidence, it seems to fit most data available on the photooxidation of polyolefins. Many complicating factors enter into photooxidative reactions of commercial polymers, however, as a result of impurities and structural irregularities that are usually present. Singlet oxygen and ozone have been suggested[76] as possible initiators of photooxidation. Traces of residual catalyst or added stabilizers may influence the mechanism as proposed for unmodified polyolefins.

Thermal oxidation, specifically autoxidation and photooxidation as a component of outdoor weathering are the two most general types of degradation affecting all polymers. In addition to these, there are several other types of degradation which take place under unusual conditions, or which affect only a limited number of polymers. Since these degradation reactions have a lesser impact on general applications, they have not been investigated to the same extent as thermal or photooxidation. High-energy radiation contributes to polymer degradation when polymers are exposed to intense radiation from natural or artificial sources. The increasing use of polymers in extraterrestrial applications and exposure near nuclear reactors are representative of these two environments.

When polymers are exposed to high-energy radiation, the initial reaction is a homolytic scission of bonds to form free radicals. When the ruptured bonds are those between substituent groups on the backbone chain, small molecular fragments are formed and if these diffuse away from the macroradical, recombination is not possible. When carbon-to-carbon bonds along the backbone chain are cleaved, however, the fragments are large radicals which are held in close proximity by a cage effect caused by the surrounding polymer mass. There is then a high probability for recombination. However, if oxygen is available, reaction with the initial radicals is likely to occur so that the backbone chain of carbon-to-carbon bond cannot reform. This reaction is important in the radiolytic reactions, but only in terrestrial applications. In space, there is little or no oxygen available for these secondary reactions.

Formation of ethylenic unsaturation during radiolysis has been attributed[79] to elimination of molecular hydrogen in a single step as represented in the radiolysis of polyethylene,

$$\sim CH_2 - CH_2 - CH_2 - CH_2 \sim \xrightarrow{\text{Radiation}} \sim CH_2 - CH = CH - CH_2 \sim + H_2$$

Formation of molecular hydrogen may also result from the following two-step reaction mechanism,

$$\sim CH_2 - CH_2 - CH_2 - CH_2 \sim \xrightarrow{\text{Radiation}} \sim CH_2 - \dot{C}H - CH_2 - CH_2 \sim + H^{\bullet}$$

$$H^{\bullet} + \sim CH_2 - CH_2 - CH_2 - CH_2 \sim \longrightarrow \sim CH_2 - \dot{C}H - CH_2 - CH_2 \sim + H_2$$

Coupling of macroradicals leads to the formation of cross-linked polymers.

$$\sim CH_2-\dot{C}H-CH_2-CH_2\sim + \sim CH_2-\dot{C}H-CH_2-CH_2\sim \longrightarrow \begin{matrix}\sim CH_2-CH-CH_2-CH_2\sim \\ | \\ \sim CH_2-CH-CH_2-CH_2\sim\end{matrix}$$

Extensive cross-linking during radiation can lead eventually to gel formation. It has been suggested[80] that chain scission to produce unsaturated products occurs as follows

$$\sim CH_2-\underset{}{\overset{CH_3}{\overset{|}{C}H}}-CH_2-CH_2-CH_2\sim \xrightarrow{\text{Radiation}} \sim CH_2-\overset{CH_3}{\overset{|}{C}H}=CH_2 + \dot{C}H_2-CH_2\sim$$

There has been an interesting development reported by Bovey et al[81] in the radiolysis of crystalline structures with a chain-folding orientation. In these crystals, molecular chains are folded with fixed spacing between folds. High-energy radiation might be expected to form cross-links if the spacing is favorable, but there is little or no flexibility in the crystallites. If cross-linking cannot take place, then scission would be the likely reaction. When crystals of the model hydrocarbon, $C_{44}H_{90}$, were exposed to gamma radiation of 53 Mrad with ^{60}Co at 25°C, there appeared to be no chain scission. Instead gel permeation chromotgraphy showed that about one percent of the molecules had doubled in molecular weight.

Each of the radiolysis reactions discussed to this point could lead to polymer degradation, without subsequent reaction with oxygen. When oxygen is present, as is like in all but extraterrestrial applications, the initial macromolecules undergo reaction much the same as those described in thermal oxidation. Peroxy radicals form which then abstract hydrogen from the same or other polymer molecules in a typical radical initiated, chain mechanism.

The reaction of ozone with stressed, unsaturated elastomers has been studied extensively because of its importance in the degradation of natural rubber. This reaction limited to those elastomers having ethylenic bonds in their backbone chain and or when they are under mechanical stress. Ozonolysis is the primary reaction in this type of degradation which is not believed to be free-radical in nature[82]. The degradation of rubber by ozone has been studied by many investigators[83-85]. Ozone has been discussed previously as it exists in the upper atmosphere, providing a filter for uv radiation below 290 nm. There is also a significant concentration of this highly reactive form of oxygen near the earth's surface, particularly in urban and industrial areas. The effect of ozone on rubber under stress is observed as surface cracks which are always perpendicular to the direction of applied stress. When a bioxial stress is applied, the surface develops a pattern of small squares. As reaction proceeds, these cracks may propagate through the polymer, eventually causing fracture. Failure could then result from loss in mechanical strength or in surface appearance.

Mechanical energy in the from of applied stress promotes several types of polymer degradation in addition to its role in ozone-induced reactions. High levels of mechanical energy can cause the rupture of polymer bonds. This occurs when elastomers are masticated under high stress. Radicals formed as bonds are ruptured, and the resulting degradation causes changes in chemical structure and in mechanical properties. In the presence of oxygen, the initial radicals react rapidly to form peroxy radicals. Typical oxidative-chain reactions then follow. Mechanical stress has also been shown to accelerate oxidative degradation of polyolefins[86].

Solvent crazing of stressed polymers is sometimes considered as a type of degradation. In contrast to environmental stress cracking, however, solvent crazing can be reversed if the applied stress is removed quickly[87]. The rate at which crazing occurs is also dependent on the level of applied stress[88]. When the stress is not removed quickly, solvent crazing cannot be reversed, and degradation results.

Polymers which are synthesized by condensation reactions are particularly susceptible to degradation by hydrolysis. Random scission of bonds along the backbone chain can occur as in,

$$R-N(H)-C(=O)-R^{\cdot} \xrightarrow{H_2O} R-NH_2 + {}^{\cdot}HO-C(=O)-R^{\cdot}$$

Poly(methyl methacrylate), on the other hand, is an addition-type polymer, which undergoes hydrolytic degradation without chain scission, reaction taking place at ester bonds on substituent groups. Hydrolysis may be catalyzed by either acids[89] or bases[90], and additional catalysts may form within the polymer as a result of accompanying thermal degradation. Polyamides, polyesters, polycarbonates, and polysaccarides are among the important, commercial polymers that are degraded by hydrolysis. As in other types of degradation discussed previously, there are important differences among polymers in their stability to hydrolysis. Nylon 1,1 has a longer hydrocarbon segment than 6,6 nylon and is therefore more resistant to hydrolytic degradation. The rate of hydrolysis is also limited by the diffusion of water into the polymer bulk. For significant reaction to occur, water must be absorbed at the surface and then permeate into subsurface regions. Flexibility of polymer chains also contributes to hydrolytic instability[91] by opening the structure to moisture penetration. Hydrolysis is believed to occur primarily in amorphous regions[92] which are more readily penetrated by water molecules.

There are two general approaches to the stabilization of polymers. (1) by modification of molecular structure and (2) by the use of additives. Dependent on the mode of degradation, either or both of these techniques may be employed. When the initiation rate is low, additives can be effective and radical traps or chain terminators may be useful under these conditions[93]. At high initiation rates, additives are less effective, and stabilization by structure

modification may be the only practical approach. Additives would be overwhelmed by the large number of radicals formed during initiation.

Thermal degradation in the absence of oxygen (pyrolysis) usually takes place at elevated temperatures. The initiation rate is high and therefore additives are not so effective as in the inhibition of low-temperature oxidation or photooxidation. Structural modification in which relatively weak bonds are replaced by bonds of higher dissociation energy is the preferred approach. There is wide variation in the stability of polymers to nonoxidative thermal degradation. This can be attributed to differences in the dissociation energies of those by which make up the structure. At elevated temperatures, bonds may cleave along backbone chain in a random-scission process or by depolymerization. In other polymers, substituents are split off from the backbone chain. Whatever the mechanism of pyrolysis, it is evident that replacement of weak bonds with others having a higher dissociation energy will increase thermal stability. This approach has been applied successfully in a limited number of cases in which weak links or labile substituents are responsible for initiating degradation. Replacement of a few such bonds can usually be accomplished without altering the original polymer beyond acceptable limits.

It has long been suspected that structural defects in poly(vinyl chloride) (PVC) responsible for the poor thermal stability of this important polymer. Various investigators have suggested terminal chlorine, alkene groups, branched points, head-to-tail structures, and irregularities formed during prior oxidation as potential initiation sites. Identification of the exact defect structures responsible for initiation of the thermal degradation of PVC, however, has not as yet been established. Several reviews[94-97] deal with the relative importance of suggested structural defects on the thermal degradation of PVC. Though the weight of evidence supports structural defects as the primary initiation sites, the possible contribution of normal repeating units cannot be neglected[97-100]. Nonetheless, prior reactions of PVC which could remove labile groups is an

attractive possibility for stabilization in that the splitting off of hydrogen chloride would be suppressed. This is in contrast to the more conventional mechanisms for stabilization of PVC in which basic additives are used to neutralize hydrogen chloride which is now generally agreed to be a catalyst for PVC degradation.

In 1959 Frye and Horst[101] proposed a mechanism for stabilization of PVC using organometallic stabilizers. However, attempts to demonstrate the addition of ligands from the stabilizer to PVC molecules were not successful at first, and the theory did not find wide acceptance. Starnes and coworkers[102,103] reasoned that insufficient stabilizer had been used in previous experiments and that the reaction might not proceed readily in the molten polymer. These investigators studied the reaction of PVC in o-chlorobenzene solution with a large excess of di(n-butyl)bis(n-dodecylthio) stannate as the stabilizer. Sufficient stabilizer was used to react with all of the reactive sites believed to be present, and the reactions were carried out at temperature up to 185°C. Under these conditions, it was found that reactions proposed by Frye and Horst did indeed take place as follows,

$$\sim\!\sim CH_2 - \underset{H}{\overset{Cl}{C}} - CH{=}CH \sim\!\sim \quad + \quad \underset{(MLCl)}{ML_2} \longrightarrow$$

$$\sim\!\sim CH_2 - \overset{L}{CH} - CH{=}CH \sim\!\sim \quad + \quad \underset{MLCl_2}{MLCl}$$

in which M is $(C_2H_5)\,Sn^{+2}$ and Y is $C_{12}H_{25}S^{-}$. Similar results were obtained with Ba^{+2}, Cd^{+2}, Zn^{+2}, Pb^{+2} as the metal and with RS^{-} , RCO_2 or RO^{-} as the organic anion. Thermal stability of the modified PVC was increased up to ninefold by replacement of labile chlorines, and stability increased with amount of ligand bonded to the polymer. Thus structural modification of PVC has been shown to be an effective method for stabilizing this sensitive polymer against thermal degradation. Although evidence has been reported suggesting the presence of

weak links in other polymers, as in radical-polymerized polystyrene[104], these bonds appear to be in the backbone chain. Replacement of such week links would require a major alteration in structure of the polymer.

There are several important examples in which thermal stability has been improved by copolymerization of the primary monomer with traces of a comonomer. Endcapping of the terminal hydroxyl group in polyoxymethylene (POM) is one such example having considerable commercial importance. Formaldehyde reacts spontaneously to form a low-molecular- weight oligomer. Although it had been known for some time that macromolecules could be produced from formaldehyde, the homopolymer degraded rapidly once removed from the reaction environment. Depolymerization is initiated at chain ends as indicated by the inverse relationship[105] between stability and molecular weight in these polymers. As a result, the excellent mechanical properties anticipated in the high- molecular-weight polymer could not be realized. In 1956, however, reactions were developed[106] in which the terminal hydroxyl group was converted to either an ester or an ether group. Depolymerization was inhibited by this structural modification, and polyoxymethylenes became available commercially[107,108].

Reaction with acetic anhydride is typical of this structural modification,

$$\sim\sim CH_2 - O - CH_2 - OH + (CH_3CO)_2 \longrightarrow$$

$$\sim\sim CH_2 - O - CH_2 - O - CO - CH_3 + CH_3COOH$$

Although these reactions prevented depolymerization initiated at chain ends, random scission could still take place. Depolymerization would then proceed from the point random cleavage with eventual reversion back to monomer. To minimize this problem formaldehyde has been copolymerized[109] with small amounts of various commoners including ethylene oxide. Even when random chain cleavage occurs in these copolymers, depolymerization stops when the first commoner unit is reached. Although there would be some

degradation with a loss in mechanical strength, the effect would not be as savere as in POM polymers with only endcapping. Modified polyoxymetylenes are used in many applications because of their superior strength and clarity.

Poly(methyl methacrylate) (PMMA) is an important polymer used extensively in decorative applications and as a glazing material. The homopolymer, however, degrades rapidly at elevated temperatures, depolymerizing to monomer in 95% yield. Poly (methyl acrylate) (PMA), on the other hand, is much more resistant to depolymerization. Random copolymers of methyl methacrylate and methyl acrylate should be better thermal stability than PMMA since depolymerization would not proceed readily once a methyl acrylate unit is reached. Copolymers with varying amounts of two monomers have been made [110], and although the anticipated improvement in stability was realized, other important properties of PMMA were sacrificed.

Thermal stability and degradation products of the homopolymers of 2,3-dibromopropyl methacrylate and 2,3-dibromopropyl acrylate and their copolymers with methyl methacrylate, methyl acrylate, and styrene have been described and discussed by Grassie and Diab[111-115], by using thermal volatilization analysis (TVA) technique. The effect of bromine-containing comonomers on the products and mechanisms of degradation of some common polymers with a view to a better understanding and control of the fire hazard associated with their application.

Homopolymer of acryloyl chloride (AC) and its copolymers with methyl methacrylate and methyl acrylate have been given a great of attention in the last few years[57,116,117]. Their stability and degradation products have been of particular interest. The copolymers are less stable than poly(methyl methacrylate) and poly(methyl acrylate) homoplymers. The activation energies of the decomposition of the copolymers and the reactivity ratios of the copolymerization were calculated.

The bonds forming cross-links in network polymers contribute significantly to the stability. Thus thermosets as a general class have greater resistance to heat than do thermoplastics. Cross-linking can be considered as special type of structural modification. The excellent heat resistance of melamine-formaldehyde polymers enables thermoset resins to used in applications such as counter tops where high temperatures may be encountered. Thermosets formed from formaldehyde and urea also have excellent thermal stability. Surface cross-liking of poly(vinyl chloride) by radiation forms a product having both outstanding mechanical strength and good thermal stability[118].

Some polymers designed for high-temperature resistance take advantage of the inherent stability of network structures. When a single covalent bond in a thermoplastic is broken, chain scission occurs, but in the densely crosslinked structures many bonds must be broken before extensive degradation take place. Polymers with very high heat resistance have been used as ablation shields to protect space vehicles during re-entry into the earth' s atmosphere. Many of these specialized polymers have a highly cross-linked or ladder structure[119]. A typical structure for a ladder polymer based on silicon would be,

C_6H_5 C_6H_5 C_6H_5 C_6H_5
Si O Si O Si O Si O
O O O O
Si O Si O Si O Si O
C_6H_5 C_6H_5 C_6H_5 C_6H_5

Heat resistant polymers are designed to withstand temperatures above 300°C for extended periods and much higher temperatures for shorter exposures.

Thermal degradation in the absence of oxygen usually takes place at higher temperatures than oxidative degradation. The initiation rate is higher at elevated temperatures and as a result additives are less effective. Added stabilizers would require high mobility to reach sites of incipient degradation, and would have to be present in high concentration in order to react with the large number of radicals produced under these conditions. Despite these restrictions, additives can perform at least a minor role in stabilization against thermal degradation. Additives may inhibit thermal degradation by modifying relatively weak bonds under elevated temperature conditions to form bonds with higher dissociation energies. Such reactions are highly specialized and have only limited application. These reactions would be different from prior treatment of ploy(vinyle chloride) to replace labile chlorines. Alternatively, an additive could function as a chain terminator. In thermal degradation, however, chain reactions do not play the dominant role that they do in low-temperature oxidations. Additives are useful when oxidation takes place simultaneously with thermal degradation.

Only decades ago polychelates derived from polymeric ligands and transition metal ions attracted the attention of many investigators. Review of the literature' s reveal that the reaction of metal ions with polymer containing pendant functional groups produces coordinated systems possibly having enhanced thermal stability and thereby having improved chemical resistance[120-123].

Poly(8-quinolyl acrylate) (P8-QA) and polymers of the complexes of 8-quinolyl acrylate (8- QA) with some transition metal bromides and uranyl acetate have been prepared and characterized by elemental analyses, electronic and vibration spectroscopic studies and magnetic moment measurements[124]. It was found that dioxouranium (VI) acetate reacted with 8-QA monomer in a 1:3 metal:ligand molar ratio and with Cu(II), Ni(II) and Co(II) bromides in 1:2 metal:ligand stoichiometry. The thermal stabilities of the polymer complexes were studied by means of thermogravimetric analysis and

showed that 8-QA-metal bromides and 8–QA-uranyl acetate polymer complexes are more stable than P8–QA homopolymer.

Poly(2-acrylamiophenol) (PAP) homoplymer and polymer complexes of 2- acrylaminophenol (AP) with Cu(II), Ni(II), Co(II) and Cd(II) chlorides and uranyl acetate were prepared and characterized by Diab et al[125]. It was found that AP reacted with Cu (II) and Cd (II) in 1:1 molar ratio and with Co(II), Ni(II) and uranyl ion in 2:1 molar ratios. The stability of the polymer complexes increases in the order PAP-uranyl acetate > PAP-$NiCl_2$ > PAP- $CoCl_2$ > PAP homopolymer > PAP-$CdCl_2$ > PAP-$CuCl_2$. This sequence could be due to the formation of stable 5-membered chelate ring in case of PAP-uranyl acetate, PAP- $NiCl_2$ and PAP-$CoCl_2$.

It was found that[126], ploy(2-acrylaminopyridine) (PAPy) form a 1:1 molar ratio with Cu(II) and Cd(II) chlorides and with Ni(II) and Co(II) chlorides in a 2:1 molar ratio. The stabilities are found to be in the order PAPy-$CuCl_2$ > PAPy-$CdCl_2$ > PAPy- $NiCl_2$ > PAPy-$CoCl_2$ > PAPy homoplymer. The greater stability of the polymer complexes than the homopolymer may be due to the formation of stable 6- membered chelate ring in these complexes.

Recently, poly(4-vinyl pyridine) homopolymer and its complexes with $CuCl_2$, $CoCl_2$ and $NiCl_2$ have been prepared and characterized by elemental analyses, electronic and vibration spectroscopic studies and magnetic moment measurements[127]. The thermal stabilities of the homopolymer and its complexes were studied by thermogravimetric analysis and it was found that polymer complexes show greater stabilities than the homoplymer, due to the formation of stable 6- or 5-membered ring structures.

The effect of some neutral polymers on the physical stability of dimyristoyl-phosphatidylcholine (DMPC)-liposomes and on the phase transition parameters of phospholipid membrane was studied by size distribution measurements and differential scanning calorimetry [128]. It was shown that

uncharged macromolecules can be effective steric stabilizers for the vesicles. A close correlation was found between the thickness of the polymer layer formed around the vesicles and the physical stability of the liposomes. DSC measurements confirmed that the macromolecules interact with the membrane bilayer. The best steric stabilizer, ploy (vinyl alcohol- vinyl butyral) copolymer eliminates pretransition of the membrane.

AIM OF THE WORK

Thermal stability of polymers have been given a great deal of attention, due to their commercial importance and degradation products. Stabilization of polymers could be approached by structural modification, copolymerization, crosslinking and the use of additives.

The aim of the present work includes the preparation of new monomers, namely, phenyl acrylamide (PA) and p-tolyl acrylamide (TA). The obtained monomers were polymerized forming the corresponding poly(phenyl acrylamide) (PPA) and poly(p-tolyl acrylamide) (PTA) homopolymers. Coplymerization of PA and TA with methyl methacrylate (MMA) and methyl acrylats (MA) were carried out forming PA-MMA, TA-MMA and TA-MA copolymers. Five copolymers were prepared for each pair covering a wide composition range so the reactivity ratios might be determined. The Thermal stability of the formed copolymers was compared with the corresponding homopolymers and the activation energies of thermal degradation were calculated using Arrhenius relationship. The products of thermal degradation of the homopolymers and copolymers were analyzed using spectroscopic and GC-MS techniques. An interpretation of the mechanism of the degradation process of the homopolymers and copolymers is given.

CHAPTER 2

EXPERIMENTAL

CHAPTER 2

EXPERIMENTAL

2.1. Introduction:

It is well known that[93,107], the thermal stability of polymers have been improved by copolymerization of the primary monomer with a traces of comonomer.

In this Chapter, the preparation of monomers of phenyl acrylamide(PA) and p-tolyl acrylamide(TA), homopolymers of poly(phenyl acrylamide)(PPA) and p-tolyl acrylamide(PTA) and copolymers of PA and TA with methyl methacrylate(MMA) and methyl acrylate(MA) were discussed. Analytical techniques and thermal methods of analysis were described.

2.2. Materials:

Acryloyl chloride (AC) (Alderich Chemical Co., Inc.) was used without further purification. It was stored below -18° C in a tightly glass—stoppered flask.

Methyl methacrylate (MMA) and methyl acrylate (MA) (BDH Chemical Ltd.), stabilized with 0.1% hydroquinone was washed with a small amount of sodium hydroxide solution, separated with a separating funnel, distilled on a vacuum line, dried over anhydrous sodium sulphate and stored below -18° C.

2,2$^{\prime}$-Azobisisobutyronitrile (AIBN) (Aldrich Chemical Co., Inc.) was used as initiator for all polymerizations. It was purified by dissolving in hot ethanol and filtering[129]. The solution was left to cool, the pure material then being collected by filtration and dried under vacuum.

Aniline (BDH Chemical Ltd.), was purified by distillation under atmospheric pressure[130]

P-Tolidine (BDH Chemical Ltd.), was used without further purification.

All other chemicals and solvents were purified by standard procedures.

2.3. Preparation of monomers and polymers:

phenyl acrylamide (PA) and p-tolyl acrylamide (AT) monomers were prepared by the reaction of equimolar amounts of AC and aniline or p-tolidine using dry benzene as solvent in an ice bath. This process is similar to the one reported of the preparation of acryloyl hydrazine, N-(β-ethylamino)acrylamide and N-[2-(6-aminopyridino)] acrylamide[131]

Poly(phenyl acrylamide) (PPA), poly(p-tolyl acrylamide) (PTA), poly (methyl methacrylate) (PMMA) and poly(methyl acrylate) (PMA) homopolymers were prepared by refluxing the corresponding monomers with dimethylformamide (DMF) (50/50 v/v) as solvent and 0.2 w/v % AIBN as initiator for two hours. The polymer products were precipitated by pouring in distilled water. PPA, PTA, PMMA and PMA homopolymers were filtered, washed with water and dried in a vacuum oven at 40^0 C for several days.

Copolymers of PA and TA with MMA or MA were prepared using 0.2 w/v % AIBN as free radical initiator and 50/50 v/v DMF as solvent. Five different copolymer compositions of PA-MMA, TA-MMA and PTA-MA were prepared, so that the reactivity ratios might be determined. Polymerizations were carried out to about 10% conversion. The polymers were precipitated by pouring into a large excess of distilled water, filtered and dried in a vacuum oven at 40^0 C for several days.

2.4. Analytical techniques:

2.4.1. Infrared spectroscopy (IR):

Spectra were recorded on Pye Unicam SP2000 spectrometry, for the polymers or qualitative measurements of the degradation products. Liquid fractions were run in solution using $CHCl_3$ as solvent. Volatile products were recorded in the gas phase using a small gas cell with NaCl windows (15 mm).

2.4.2. Nuclear magnetic resonance spectroscopy (NMR):

^{1}H-NMR spectra were obtained using a Varian EM 390 90 MHz spectrometer with integration and 20 mg samples. The polymers were dissolved in 1 ml of $CDCl_3$. The integral obtained for each sample was used for determination of the polymer compositions.

2.4.3. Microanalysis:

Nitrogen content determination were performed by the Microanalytical Unit at Cairo University.

2.4.4. Gas chromatography-mass spectroscopy (GC-MS):

The condensable degradation products of homopolymers and copolymers were analyzed with a Saturn 2000, GC 3400 with a fused quatz capillary column of 30 m x 0.25 mm coated with methyl silicone, under programmed heating condition from 40 to 200^{0}C. The GC is interfaced with a Varian mass spectrometer.

2.4.5. Thermal methods of analysis:

a) Thermogravimetry (TG)

TG measurements were made with a Mettler TG 3000 apparatus. Finely powdered (~10 mg) samples were heated at 10°/min in a dynamic nitrogen atmosphere (30 ml /min); the sample holder was boat-shaped, 10 mm X 5 mm X 2.5 mm deep and the temperature-measuring thermocouple was placed 1 mm from the sample holder.

TG was also used for the determination of rates of degradation of the homopolymers and copolymers in the initial stages of decomposition. The activation energies were obtained by application of the Arrhenius equation.

b) Differential scanning calorimetry (DSC)

DSC curves were obtained using a Mettler TA 3000 DSC. The samples were heated at 10°/min from ambient temperature up to 500°C.

c) Thermal degradation of homopolymers and copolymers:

Samples of ~ 50 mg were heated under vacuum from ambient temperature to 500° C. The volatile degradation products were collected for qualitative analysis either by IR spectroscopy or GC-MS technique.

RESULTS AND DISCUSSION

CHAPTER 3

POLY(PHENYL ACRYLAMIDE) HOMOPOLYMER AND COPOLYMERS OF PHENYL ACRYLAMIDE WITH METHYL METHACRYLATE

CHAPTER 3

POLY(PHENYL ACRYLAMIDE) HOMOPOLYMER AND COPOLYMERS OF PHENYL ACRYLAMIDE WITH METHYL METHACRYLATE

3.1. Introduction

It is well known that the thermal stability of polymers has been improved
by copolymerization of the primary monomer with traces of a comonomer. The poor thermal stability of brominated polymers, due to the weak character of the C-Br bond, has received much attention[132,133]. Diab et al[134] reasoned that interposing other monomer units such as methyl methacrylate in the poly (β-bromostyrene) (Pβ-BS) chain would lend stability of the polymer.

In this Chapter, homopolymers of phenyl acrylamide (PPA) and methyl methacrylate (PMMA) and five different compositions of copolymers of phenyl acrylamide and methyl methacrylate (PA-MMA) were prepared, so that the reactivity ratios might be determined using ^{1}H-NMR method and the application of Fineman-Ross plots[135]. The thermal stability of the homopolymers and copolymers were examined. Thermal degradation behaviors of the homopolymers and copolymers have been studied in order to determine the nature of the degradation products and the extent to which interaction may occur between comonomer units during the degradation.

3.2. Characterization of PPA homopolymer and PA-MMA copolymers:

Phenyl acrylamide(PA) monomer was prepared by the reaction of equimolar amounts of AC and aniline in dry benzene until the evolution of hydrogen chloride ceased forming a brown powder of PA monomer (M.W. 147). Microanalysis, found N, 9.52 %. Calcd. For C_9H_9ON, N, 9.52%.

PPA homopolymer was prepared by free radical initiation of PA using 0.2 w/v% AIBN as initiator to ~10% conversion. The IR spectrum of PPA homopolymer (Figure 3.1) shows two medium broad bands at 3290 and 3441 cm^{-1} assigned to symmetric and asymmetric stretching vibrations of the amino group. The band at 1680 cm^{-1} is assigned to the antisymmetric stretching vibration of amidic carbonyl group. The bands at 1600, 1545 and 1440 $cm^{-1}$are assigned to the ν(C-H), ν (C=C) and ν (C-C) bands, respectively[136]. The C-H in plane deformation in the region 1225-1045 cm^{-1}, the ring breathing at 995 and 1005 cm^{-1}, the out-of-plane C-H deformation vibration between 775 and 750 cm^{-1} and the C-C out-of-plane deformation at 500 cm^{-1} are assigned.

The IR spectrum of PA-MMA copolymers as shown in Figure 3.2 exhibits a characteristic strong band at 1730 cm^{-1} assigned to the antisymmetric stretching vibration of carbonyl group of MMA. There is no change in the position of the bands of amino group of PA units in the copolymers.

3.3. Determination of reactivity ratios of PA-MMA copolymers:

Five different compositions of the PA-MMA copolymers with 57, 34, 24, 17 and 14 mole % PA units were prepared by free radical initiation using 0.2 w/v% AIBN and DMF (50/50 v/v) as solvent. The polymerizations were carried out to about 1 0% conversion.

The integration of ^{1}H-NMR spectrum from each sample of the copolymers was used for the calculation of copolymer composition. The monomer composition of the copolymer can be calculated from the ratio of these integrals which are proportional to the number of protons that contribute to the peaks. This method was already used for the determination of reactivity ratios for styrene-MMA[137] and methacrylate-acrylate copolymers [138]. Figure 3.3 shows the ^{1}H-NMR spectrum of PA-MMA copolymers. There are three characteristic peaks at δ 0.85-1.05, 1.88-1.94 and 2.77-2.89 ppm for CH_3, CH_2 and CH protons, respectively[139]. The amino proton at δ 7.85 ppm was

disappeared on addition of D_2O. Also, Figure 3.3 shows peak A at δ 7.15 and 7.38 ppm which is a composite peak, due to two protons in the ortho-position and three protons in meta-and para-position of the benzene ring of PA in the copolymer, respectively[140]. Peak B at δ 3.65 ppm is due to $-OCH_3$ protons of the MMA unit. Dividing the integral values due to peak A by five and peak B by three, the monomer composition of the copolymer can be calculated. By knowing the number of moles of the monomer mixture and the molar ratio of the copolymer, reactivity ratios can be calculated by means of the following equation[141]:

$$\frac{f_1(1-2F_1)}{(1-f_1)\,F_1} = \frac{f_1^2(F_1-1)}{(1-f_1)^2F_1}\;r_1 \;+\; r_2$$

Where $F_1 = \dfrac{M_1/M_2}{M_1/M_2+1}$ is the mole fraction of PA (M_1) in copolymer, $f_1 = \dfrac{n_1}{n_1+n_2}$ is

The mole fraction of M_1 in feed and r_1 and r_2 are the reactivity ratios of PA and

MMA, respectively. Figure 3.4 is a plot of $\dfrac{f_1^2(F_1-1)}{(1-f_1)^2F_1}$ versus $\dfrac{f_1(1-2F_1)}{(1-f_1)\,F_1}$ and

Figure 3.5 is a plot of $\dfrac{f_2^2(F_2-1)}{(1-f_2)^2F_2}$ versus $\dfrac{f_2(1-2F_2)}{(1-f_2)\,F_2}$ where $F_2 = \dfrac{M_2/M_1}{M_2/M_1+1}$

is the mole fraction of MMA(M_2) in copolymer and $f_2 = \dfrac{n_2}{n_1+n_2}$ is the mole fraction of M_2 in feed. From the slopes and intercepts in Figures 3.4 and 3.5 reactivity ratio values for PA-MMA copolymer are r_1 (PA)=0.21 ± 0.01 and r_2 (MMA)= 2.0 ± 0.2.

3.4. Thermal methods of analysis:

3.4.1. Thermogravimetry (TG):

TG curves of PPA and PMMA homopolymers and copolymers of PA-MMA are shown in Figure 3.6. PPA homopolymer degrades in two stages. The first starts at ~117°C with a weight loss ~45%. The second stage starts at ~333°C with a weight loss of ~44%. PMMA homopolymer degrades in two stages. The first step starts at ~260°C with a weight loss percentage of ~38%. The second degradation stage starts at ~350°C with a weight loss of ~56%. There are three TG degradation stages for all the PA-MMA copolymers. The volatilization temperatures starts at ~188, 212, 240 and 247°C for the copolymers 57, 34, 24 and 14 mole% PA units, respectively. Table 3.1 lists the percentage weight losses and the maximum rate of weight loss shown in the derivative thermogravimetry DTG. The TG curves show that the stabilities of the copolymers are intermidiate between those of the homopolymers.

To illustrate the initial stages of breakdown more clearly, a comparison study of weight loss percentage at definite temperature with copolymer composition give a clear picture on the relative stability of the entire composition range. Smooth changes in stability with composition is well demonstrated in Figure 3.7, in which the weight loss percentage at a selected temperature (250°C) using the data in Figure 3.6 is plotted against composition. The most clearly defined feature of the reaction is the increase of stability towards PMMA homopolymer. This is not the case in the thermal stabilities of vinyl bromide-methyl acrylate and β-bromostyrene-methyl acrylate copolymers[45,51], which have stable copolymers at definite compositions.

The effective activation energies of the thermal degradation of PPA and PMMA homopolymers and PA-MMA copolymers were determined from the temperature dependence of the chain rupture rate. The rate constant of the thermal degradation was plotted according to the Arrhenius relationship (Figure 3.8). Table 3.2 lists the activation energies of PPA and PMMA homopolymers

and PA-MMA copolymers. The activation energy of PPA homopolymer is smaller than that of the copolymers and PMMA homopolymer. Therefore, PPA homopolymer will undergo decomposition more readily than the copolymers and PMMA homopolymer.

3.4.2. Differential scanning calorimetry (DSC):

DSC apparatus was used for the determination of glass transition temperature (Tg) of PPA and PMMA homopolymers and PA-MMA copolymers. Figure 3.9 represents the DSC curve of 34 mole% PA units of PA-MMA copolymer and PMMA homopolymer. The Tg of PPA and PMMA homopolymers and PA-MMA copolymers are shown in Table 3.3. It seems that the values of Tg increase with increasing the mole percentage of MMA in the copolymers.

3.4.3. Thermal degradation of PPA and PMMA homopolymers and PA-MMA copolymers:

50 mg of PPA homopolymer was heated under vacuum from ambient temperature to 500°C. The volatile product of degradation was collected in a small gas cell for identification by IR spectroscopy. Figure 3.10 shows the IR spectrum of the volatile products of degradation of PPA homopolymer. The bands at 3190, 3360 and 3430 cm^{-1} are assigned to symmetric and asymmetric stretching vibration of aniline[142]. Benzene and ammonia were among the degradation products confirmed by the bands at 1490 and 2150 cm^{-1}, respectively. The liquid fractions from the degradation of the homopolymer were injected into the GC-MS apparatus. Figure 3.11 shows the GC trace for the liquid products of degradation of PPA homopolymer at 500°C. Table 3.4 gives the results of degradation products which were identified by mass spectroscopy. Some of the peaks could not be identified due to the lack of reference materials or due to the uncleared mass spectra. The numerous degradation products of PPA homopolymer indicate that the mechanism of degradation is characterized by the elimination of low-molecular-weight radicals, rather than monomer

formation in the early stage of degradation, followed by random scission mechanism along the backbone chain. It seems that the break down of PPA homopolymer occurs mainly in the C-N bond producing the radicals.

These radicals abstract $H^{\cdot}$ and produce aniline, benzene and ammonia as major products.

Compound 1 in the GC curve listed in Table 3.4 could be formed by a dimerization reaction of IV. Figure 3.12 shows the mass spectrum of compound 1.

IV

dimerization

Compound 1

m/e=186

The mass spectrum of the assignment structure 2 (Figure 3.13) is a termination reaction of the radicals III and V.

III

V

Compound 2

m/e=198

The suggested structure of compound 3 is a reaction of the assignment structure of compound 1 and carbon monoxide. Figure 3.14 shows the mass spectrum of compound 3.

H N N H + CO → Compound 3 (CHO)

Compound 3

m/e=213

Figure 3.15 shows the mass spectrum of the suggested structure of compound 4. It seems that this product of degradation is formed by a reaction between the radicals V and IV:

NH + O=C–NH → H N–C(=O)–N H

IV V

Compound 4

m/e=215

The assignment structure 5 (Figure 3.16) is a diamerization reaction of V:

2 O=C–NH → H N–C(=O)–C(=O)–N H

V

Compound 5

m/e=241

The mass spectrum of the degradation product of PPA homopolymer (compound 6) shown in Figure 3.17 was unidentified.

Figure 3.18 represents the mass spectrum of compound 7 which could be formed from the reaction of PA monomer and the radical V:

$$CH_2{=}CH{-}C(=O){-}NH{-}C_6H_5 + \dot{C}(=O){-}NH{-}C_6H_5 \longrightarrow$$

V

$$C_6H_5{-}NH{-}C(=O){-}CH_2{-}CH_2{-}C(=O){-}NH{-}C_6H_5$$

Compound 7

m/e=269

Compound 8 (Figure 3.19) is a termination reaction of IV and two radicals of III:

$$C_6H_5\dot{N}H + 2\,\dot{C}_6H_5 \longrightarrow (C_6H_5)_3N$$

IV III Compound 8

m/e=244

The mass spectrum of the assignment structure 9 (Figure 3.20) is a termination reaction of the radicals IV and VI followed by rearrangement to give the compound 9:

IV + VI →

rearrangment →

Compound 9
m/e = 262

The major mass fragments of compound 10 (Figure 3.21) give a loss of mass either 14 or 13 indicating that it is a chain polyene fragment. The degradation behavior of polyene is like polyolefines degradation[27,31] which produced chain fragments between C_6-C_{60}.

The production of MMA monomer in the thermal degradation of PMMA homopolymer reflects the general characteristics of PMMA degradation observed by Grassie[143]. A long-chain polymer radical is formed by random chain scission or by initiation at an unsaturated chain end. This radical then "unzips" to produce monomer and a similar radical:

$$\sim\sim CH_2-C(CH_3)(COOCH_3)-CH_2-\dot{C}(CH_3)(COOCH_3) \longrightarrow \sim\sim CH_2-\dot{C}(CH_3)(COOCH_3) + CH_2=C(CH_3)(COOCH_3)$$

$$\sim\sim CH_2-C(CH_3)(COOCH_3)-CH=C(CH_3)(COOCH_3) \longrightarrow \sim\sim CH_2-\dot{C}(CH_3)(COOCH_3) + \cdot CH=C(CH_3)(COOCH_3)$$

These two mechanisms explain the two TG stages of the degradation of PMMA. The first stage of decomposition is attributable to the initiation at the unsaturated chain end, while the second stage of degradation is due to random chain scission of the backbone chain of PMMA homopolymer.

The degradation gas products of PA-MMA copolymers were collected in a small gas cell for identification by IR spectroscopy. Figure 3.22 shows the IR spectrum of the volatile products of degradation of PA-MMA copolymers. Beside the characteristic bands of ammonia, benzene and aniline, there is a strong band at 1730 cm^{-1} attributed the carbonyl group of MMA monomer. GC-MS of the liquid fraction of the degradation products of PA-MMA copolymer shows similar pattern as in the PPA homopolymer. It seems that there is no interaction between the two types of monomers in the degradation of copolymers.

Table 3.1: Weight loss percentage of PPA and PMMA homopolymers and PA-MMA copolymers:

Polymer Mole%PA	Volatilization temperature, °C	First stage		Second stage		Third stage		Remaining Wt.% after 500°C
		T_{max}, °C	Wt.loss,%	T_{max}, °C	Wt.loss,%	T_{max}, °C	Wt.loss,%	
PPA	117	293	45	380	44	-	-	11
57	188	242	6	267	15	390	73	6
34	212	245	5	285	20	390	70	5
24	240	250	4	310	25	400	67	4
14	247	263	3	340	30	405	64	3
PMMA	260	297	38	350	56	-	-	6

Table 3.2: Activation energies of the thermal degradation of PPA and PMMA homopolymers and PA-PMMA copolymers

Polymer PA mole %	Activation energy(Ea) KJ /mol
PPA	71.26
57	-
34	83.14
24	98.25
17	108.7
14	111.7
PMMA	116.4

Table 3.3: Glass transition temperature (Tg) of PPA and PMMA homopolymers and PA-PMMA copolymers

Polymer Mole % PA	Tg , °C
PPA	73
57	78
34	80
24	85
17	103
14	107
PMMA	111

Table 3.4: GC-MS data of the liquid fraction of the thermal degradation of PPA homopolymer

Compound No.	Retention Time, min.	Major MS fragments	Suggested Structure (Most probable)
1	6.24	186, 171,152,140,129, 104,75, 61,47	
2	8.86	198, 166,141,115, 87, 75,61,48	
3	9.81	213, 167,150,139,129, 107,91, 75,61	

Cont'd : Table 3.4: GC-MS data of the liquid fraction of the thermal degradation of PPA homopolymer

Compound No.	Retention Time, min.	Major MS fragments	Suggested Structure (Most probable)
4	11.58	215,187,155,127,100, 85, 67, 55	
5	12.25	241,227, 213, 195, 182, 141,75,61,48	
6	13.81	257,241,227,209,199, 166, 139,112,79,65,55	unidetified

Cont'd : Table 3.4: GC-MS data of the liquid fraction of the thermal degradation of PPA homopolymer

Compound No.	Retention Time, min.	Major MS fragments	Suggested Structure (Most probable)
7	14.68	268, 259,241,227,216,188, 160, ,151,129, 101,61	N(H)–C(=O)–CH_2–CH_2–C(=O)–N(H)
8	15.36	244, 216,204,175,160, 132,107,91,65,55	$(\ )_3N$
9	16.93	262, 246,230,218,204, 160,143,129,120,84,61	H N O; O N H

Cont'd : Table 3.4: GC-MS data of the liquid fraction of the thermal degradation of PPA homopolymer

Compound No.	Retention Time, min.	Major MS fragments	Suggested Structure (Most probable)
10	17.94	301, 283,269,257,241,209, 183,129,101,61,48	Polyene structure

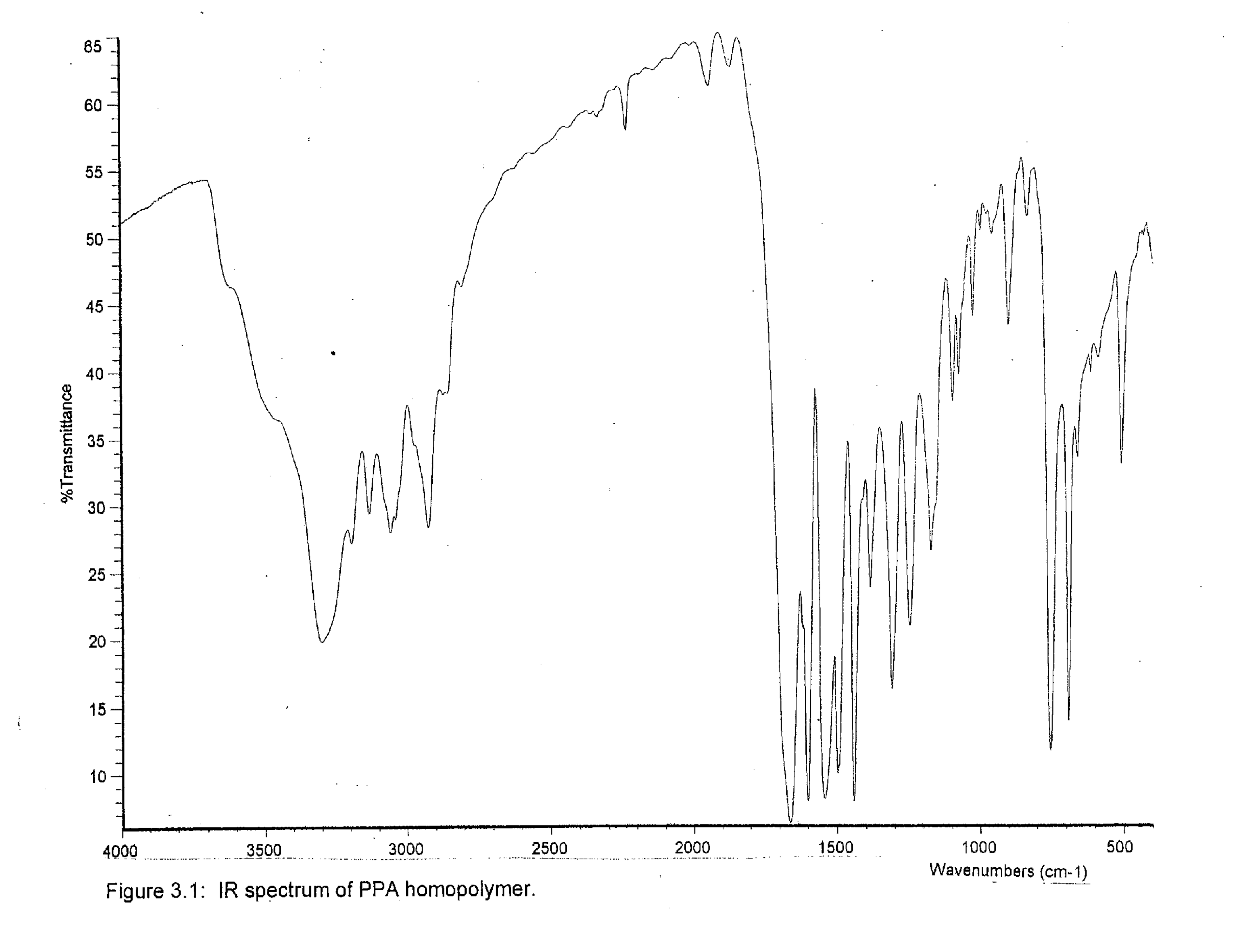


Figure 3.1: IR spectrum of PPA homopolymer.

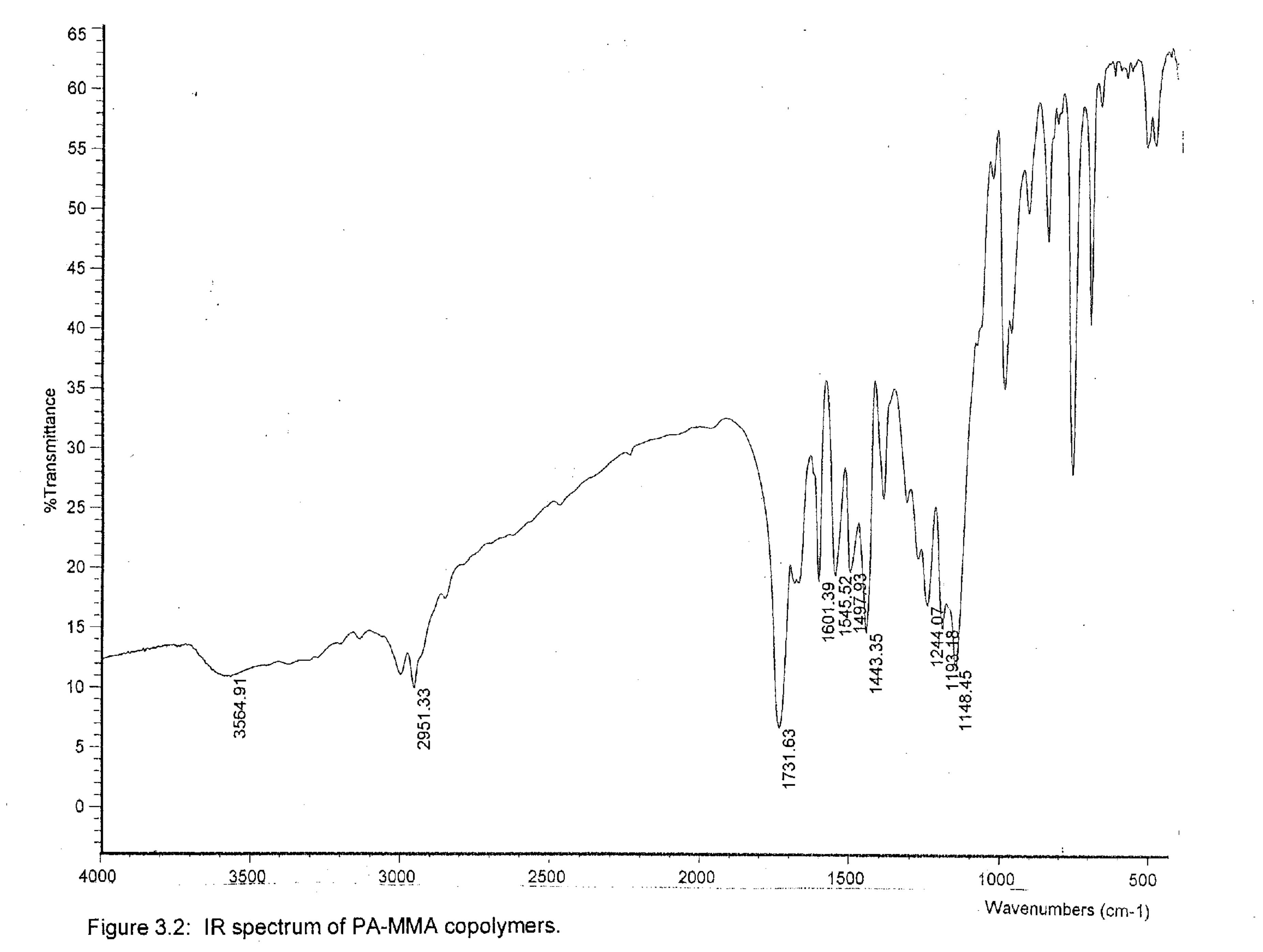


Figure 3.2: IR spectrum of PA-MMA copolymers.

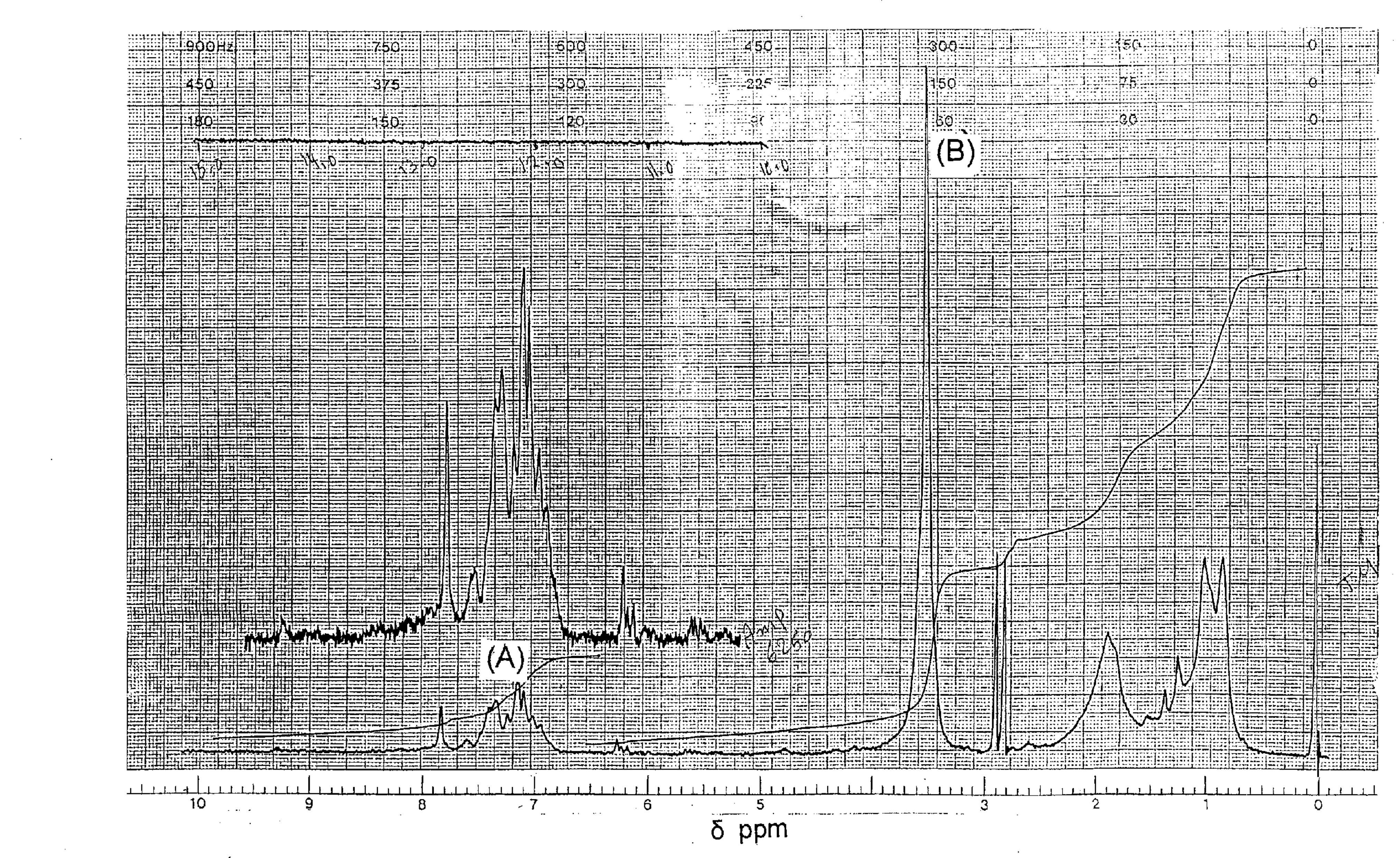


Figure 3.3: ^{1}H-NMR spectrum of PA-MMA copolymers.

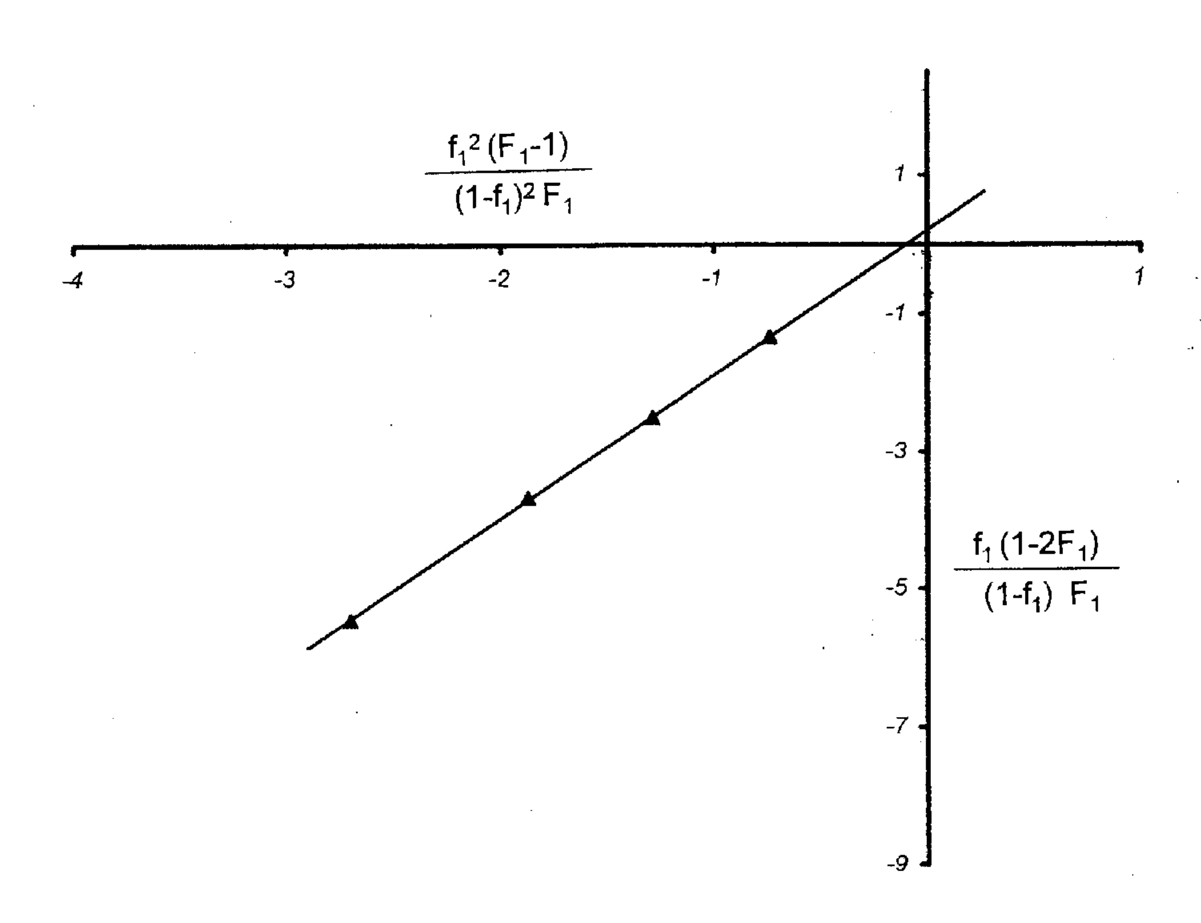


Figure 3.4: Graph of $\frac{f_1^2(F_1-1)}{(1-f_1)^2 F_1}$ versus $\frac{f_1(1-2F_1)}{(1-f_1)\ F_1}$ for PA-MMA copolymers.

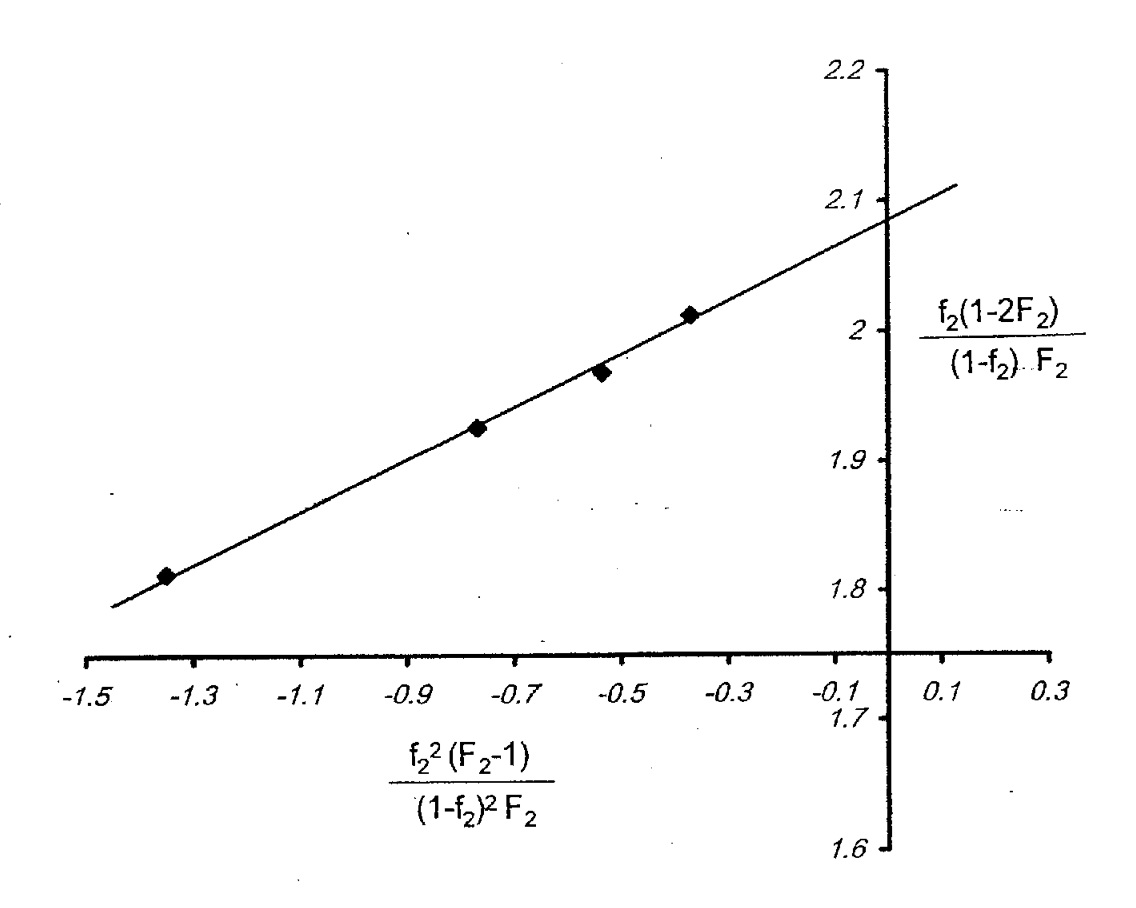


Figure 3.5: Graph of $\frac{f_2^2\,(F_2-1)}{(1-f_2)^2\,F_2}$ versus $\frac{f_2(1-2F_2)}{(1-f_2)\ F_2}$ for PA-MMA copolymers.

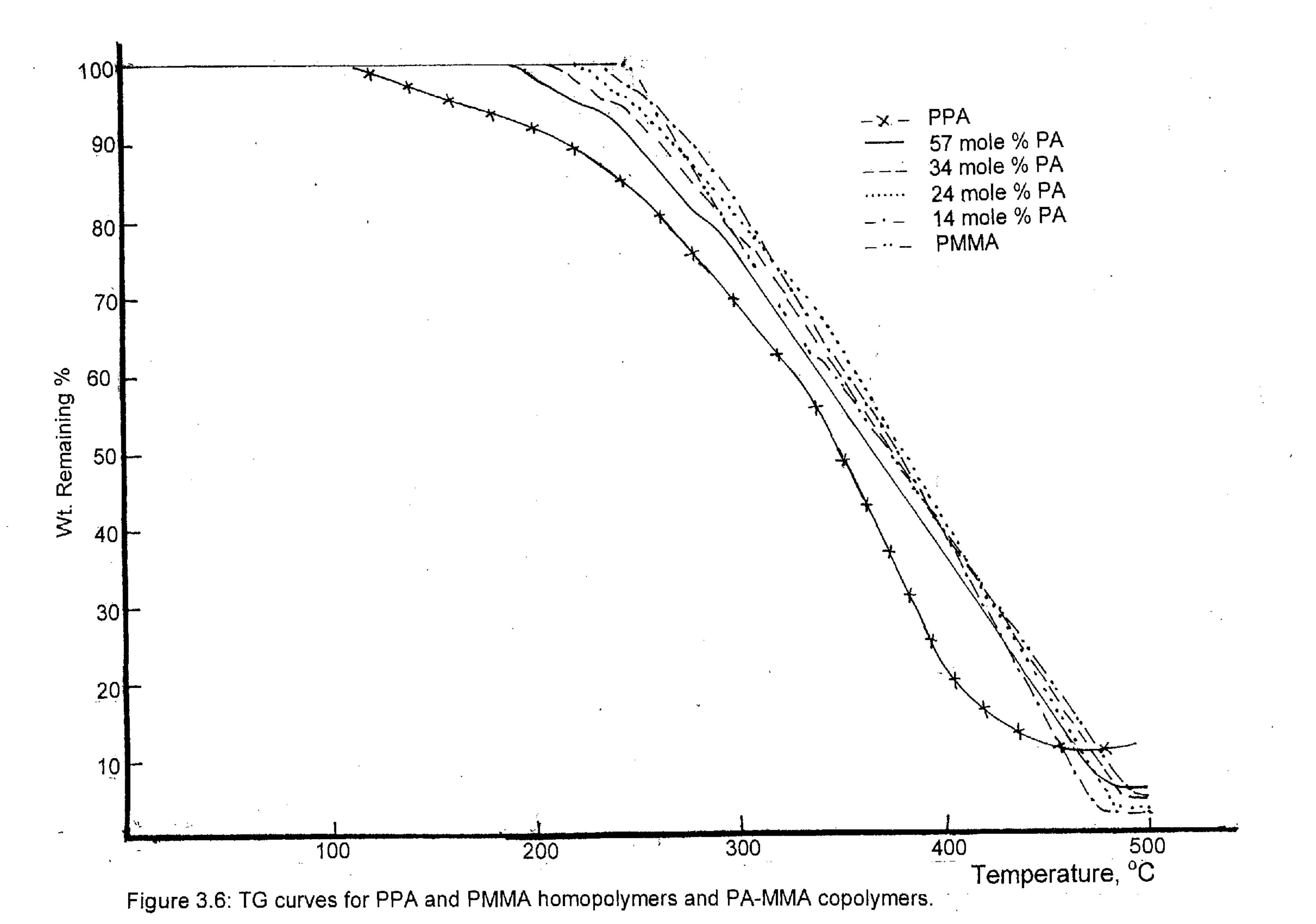


Figure 3.6: TG curves for PPA and PMMA homopolymers and PA-MMA copolymers.

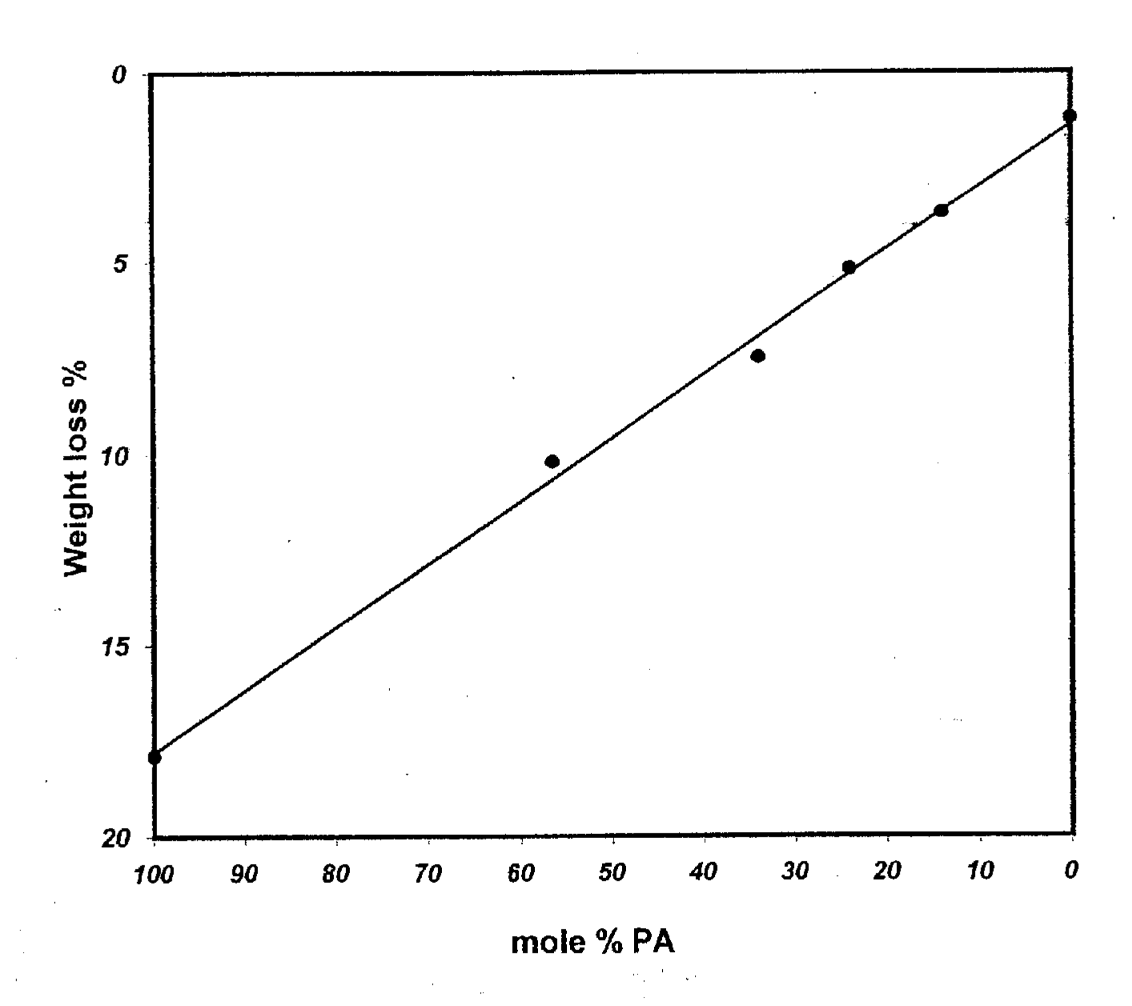


Figure 3.7: Comparison of weight loss percentage at 250 °C for PA-MMA copolymers at different compositions.

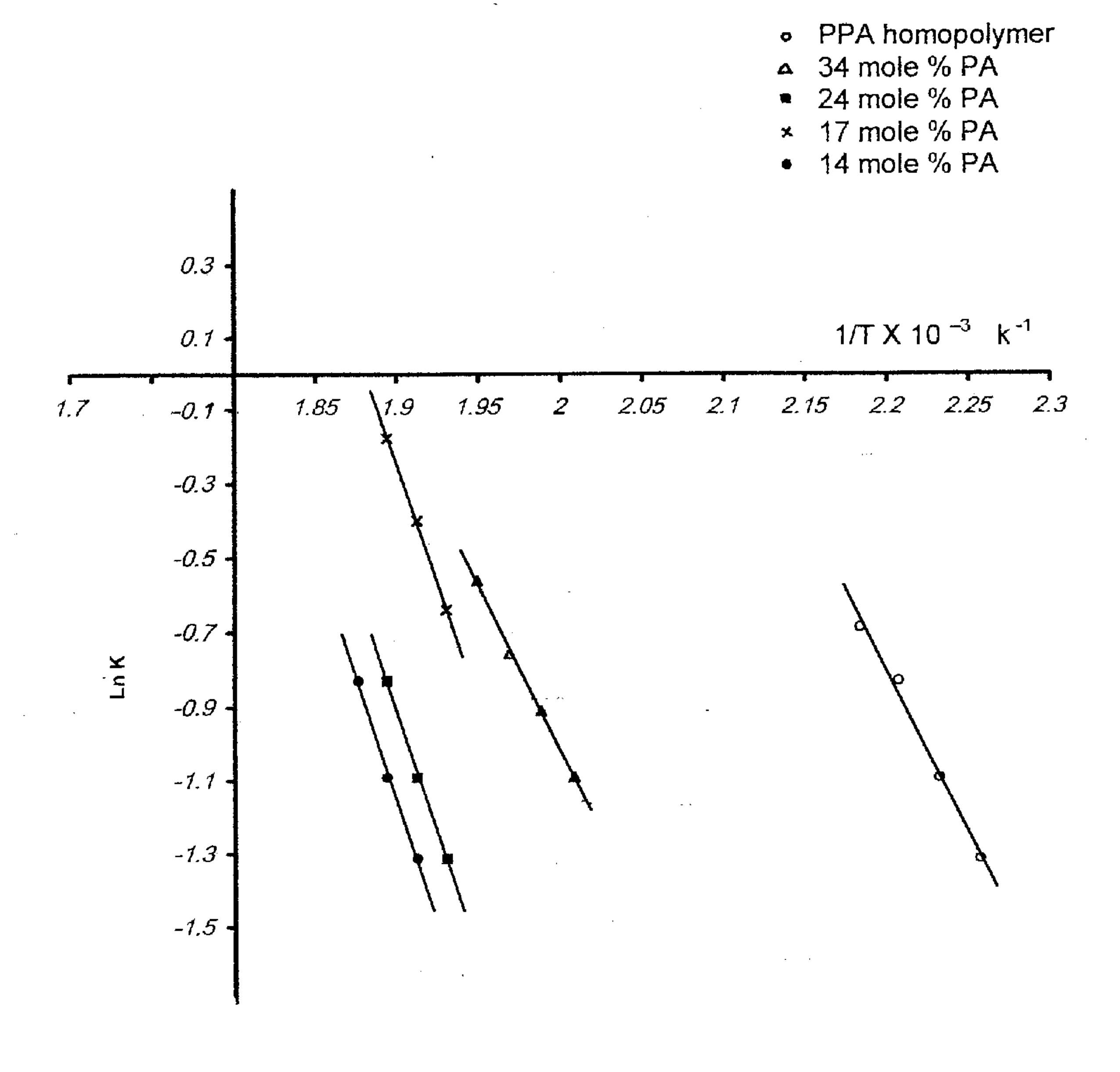


Figure 3.8: Arrhenius plots of the rate constants of degradation of PPA homopolymer and PA-MMA copolymers.

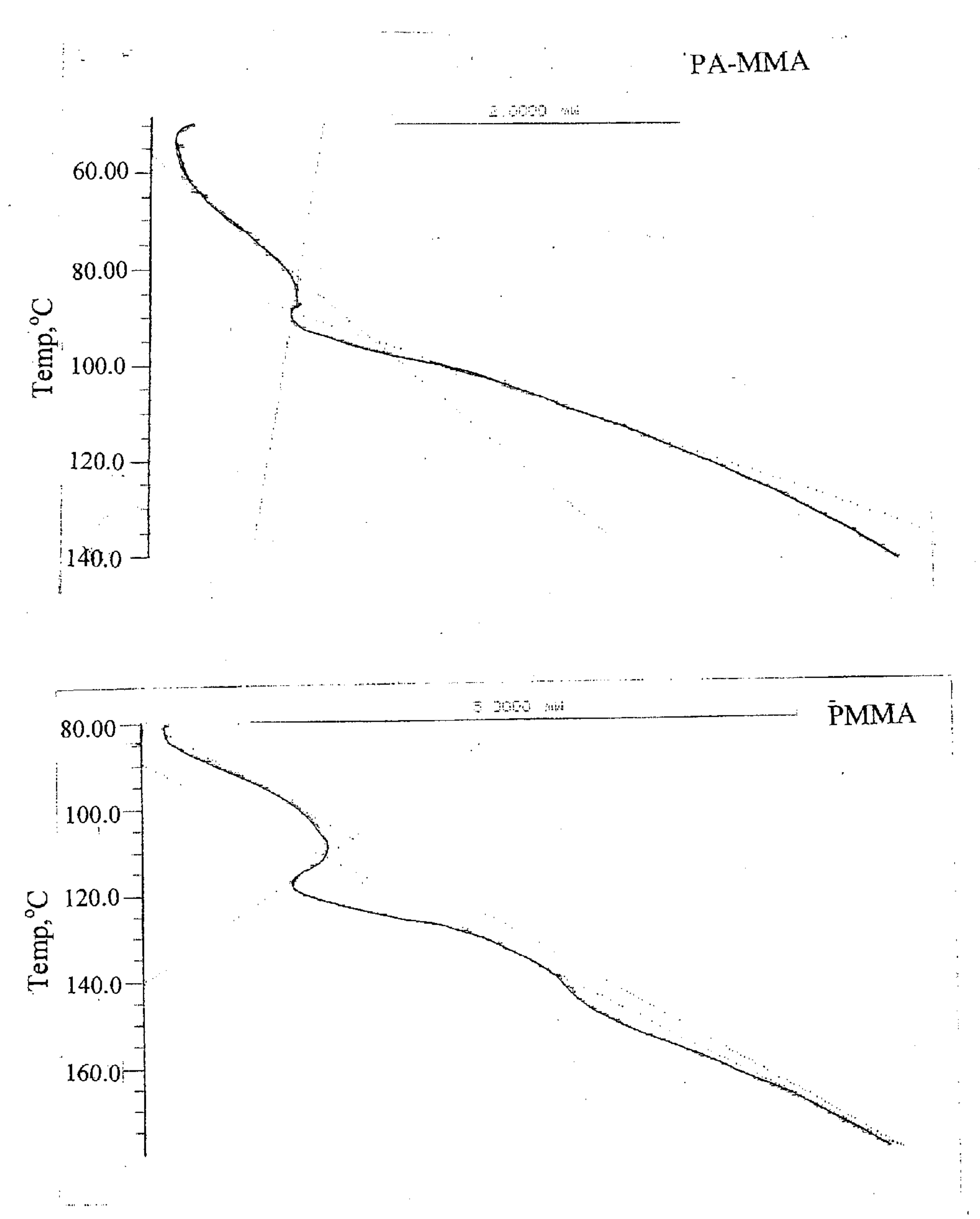


Figure 3.9: DSC curve of PA-MMA copolymer (34 mol % PA unit) and PMMA homopolymer.

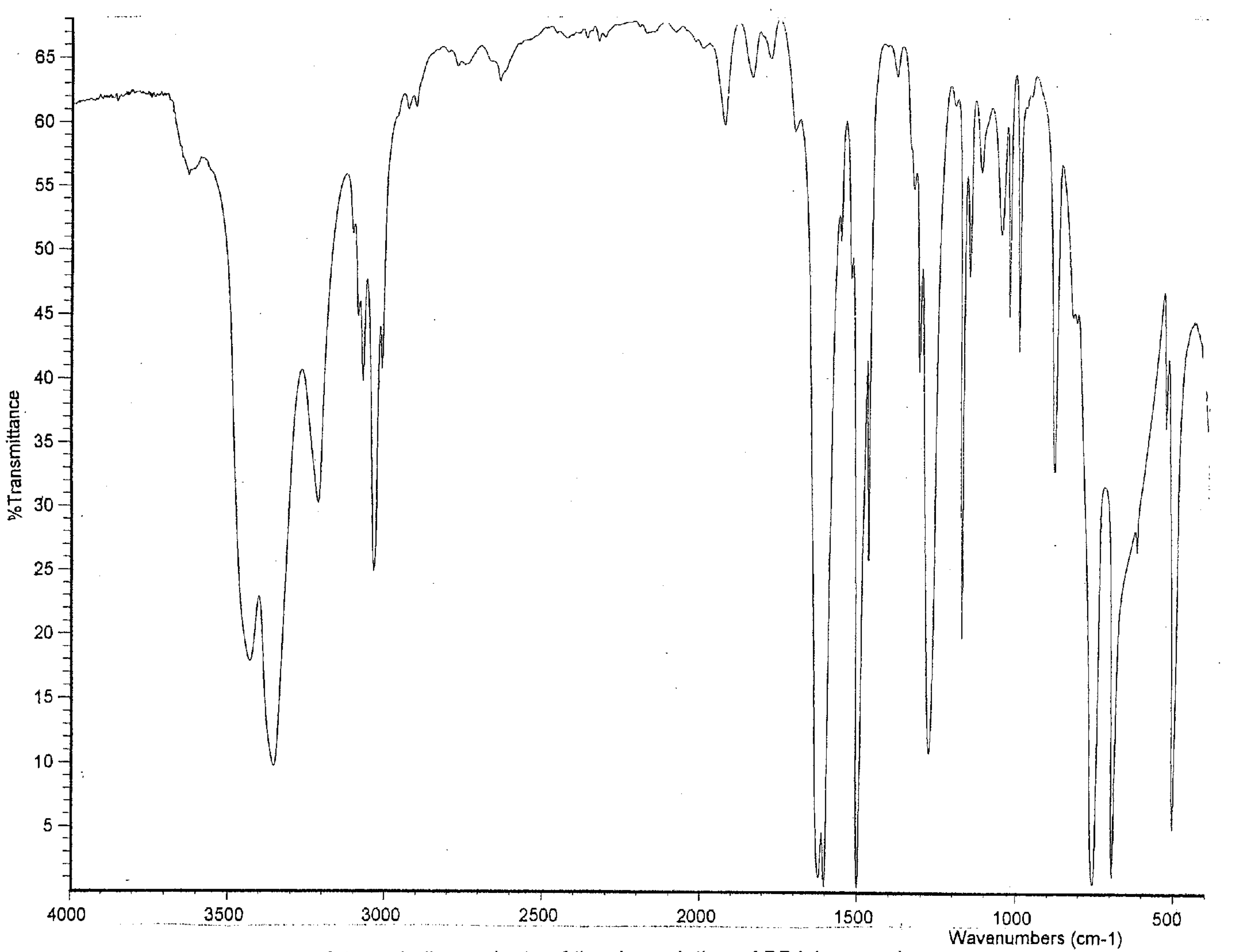


Figure 3.10: IR spectrum of the volatile products of the degradation of PPA homopolymer.

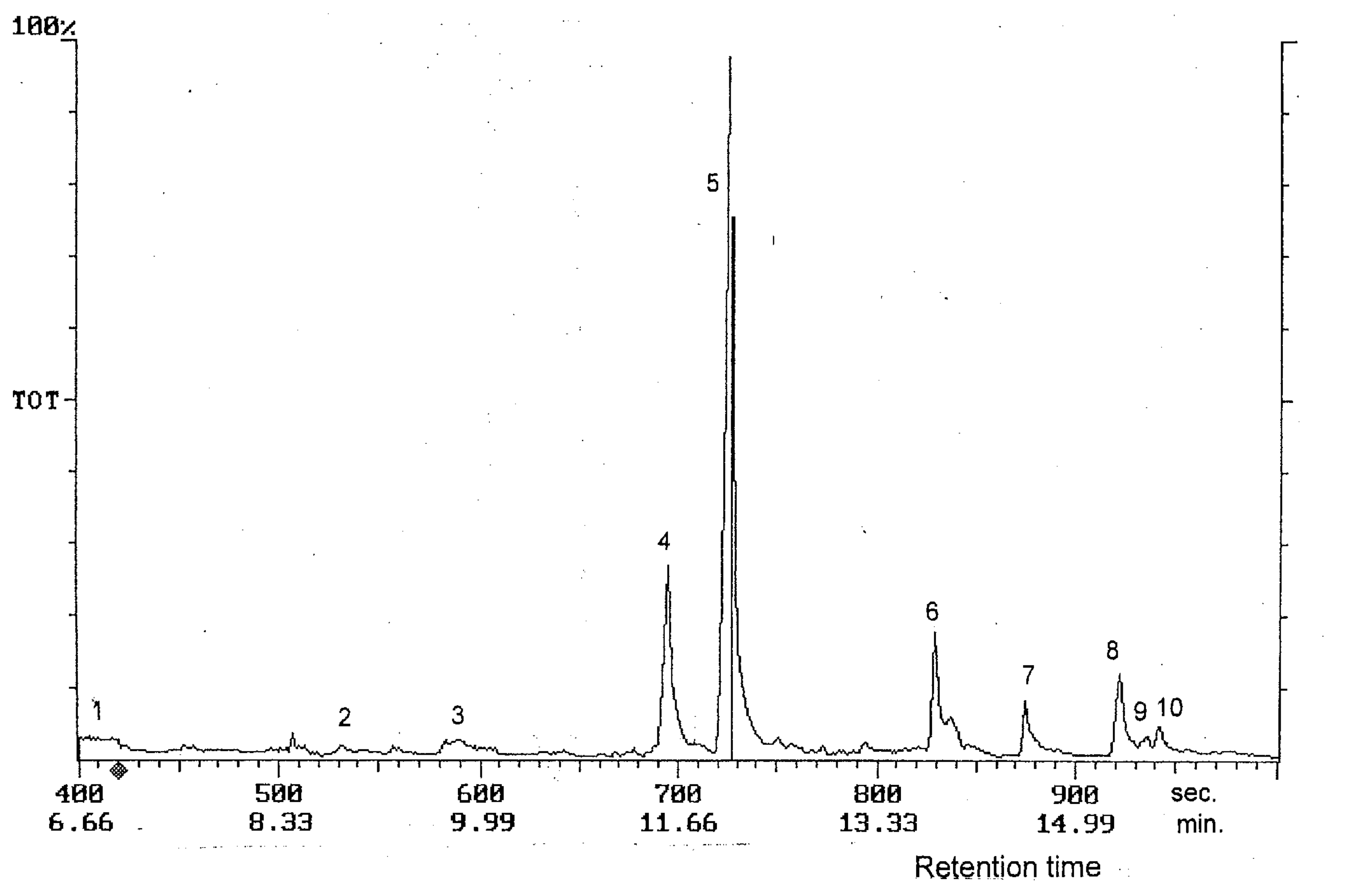


Figure 3.11: GC curve of the liquid fraction of the degradation products of PPA homopolymer.

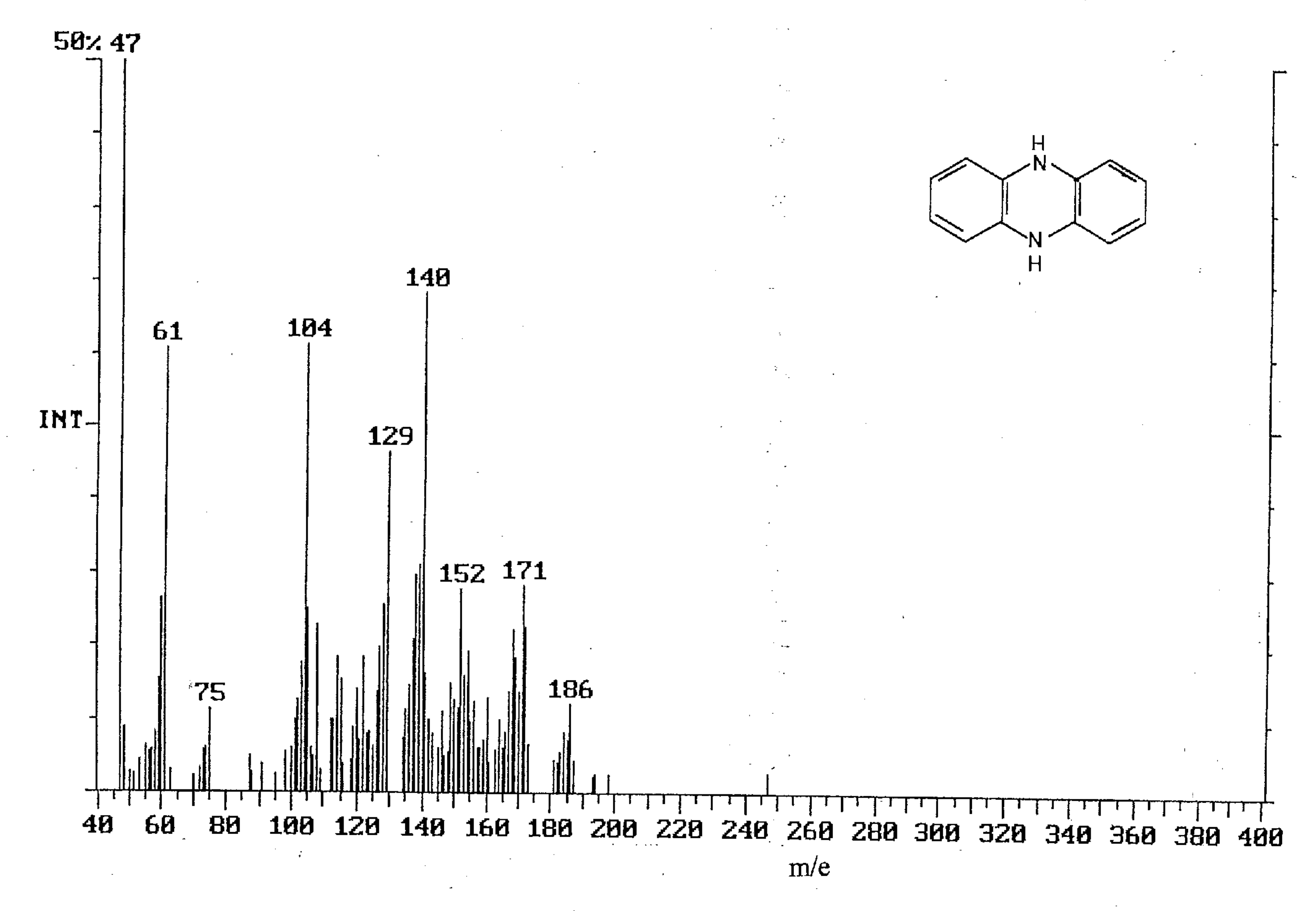


Figure 3.12: Mass spectrum of compound 1.

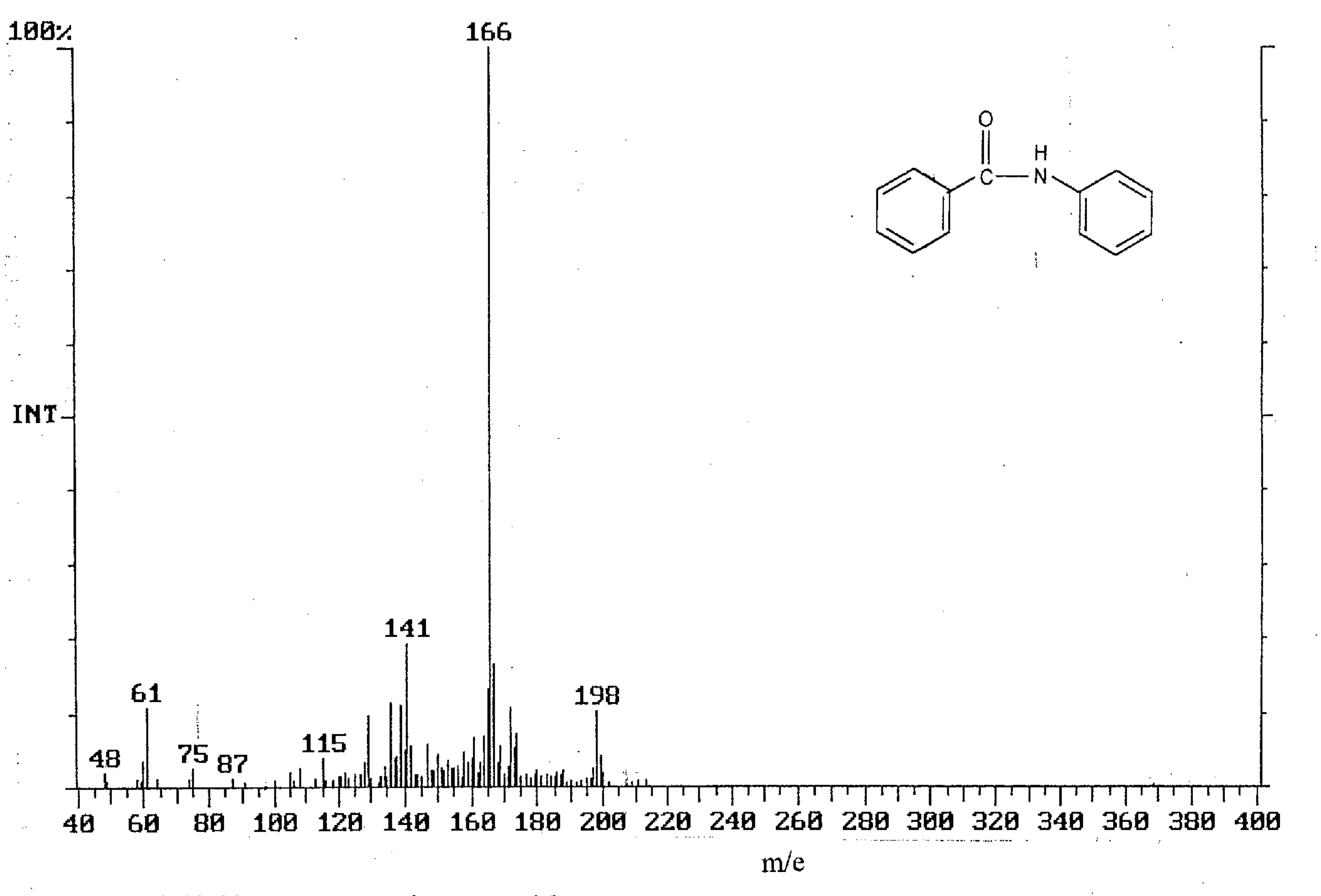


Figure 3.13: Mass spectrum of compound 2.

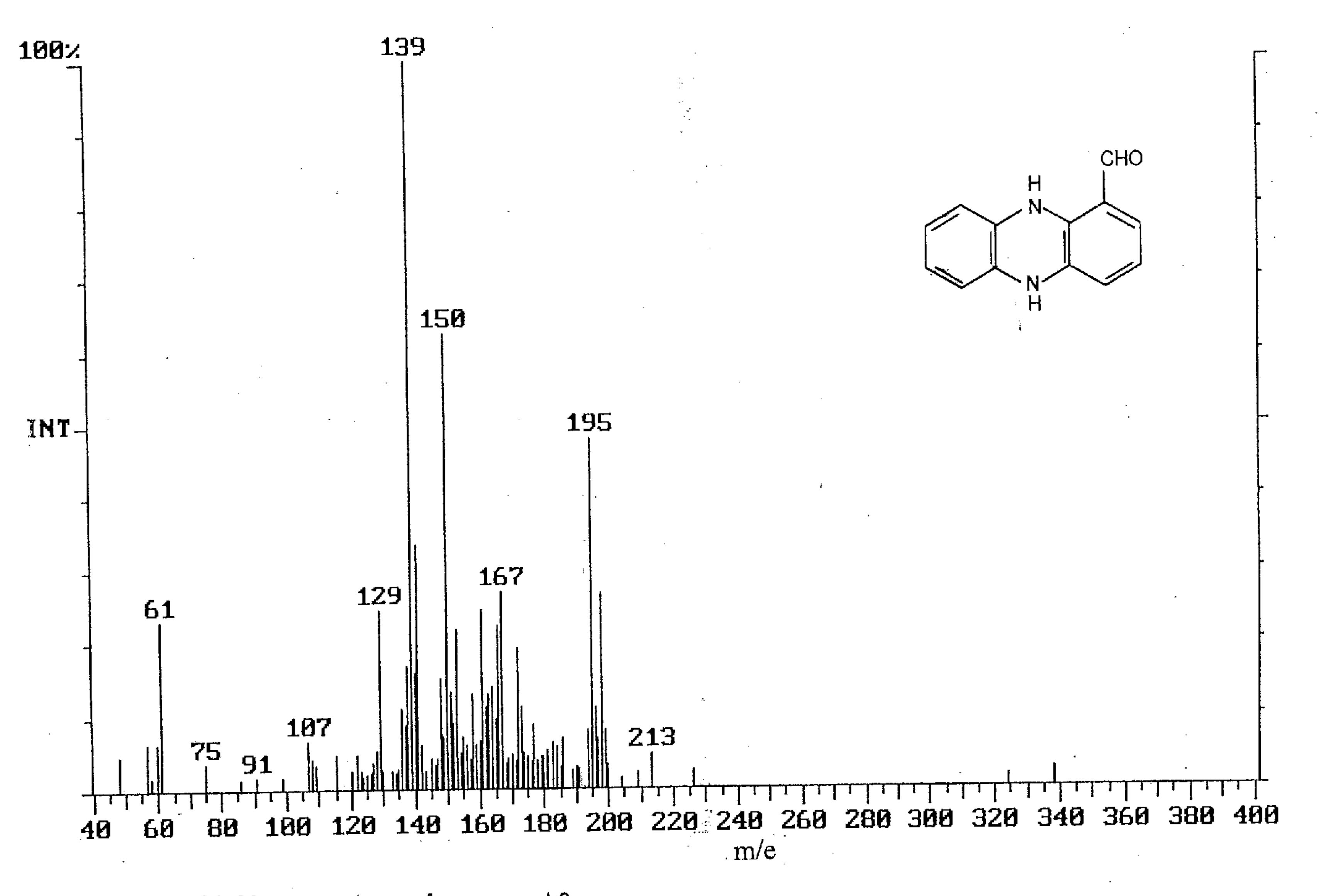


Figure 3.14: Mass spectrum of compound 3.

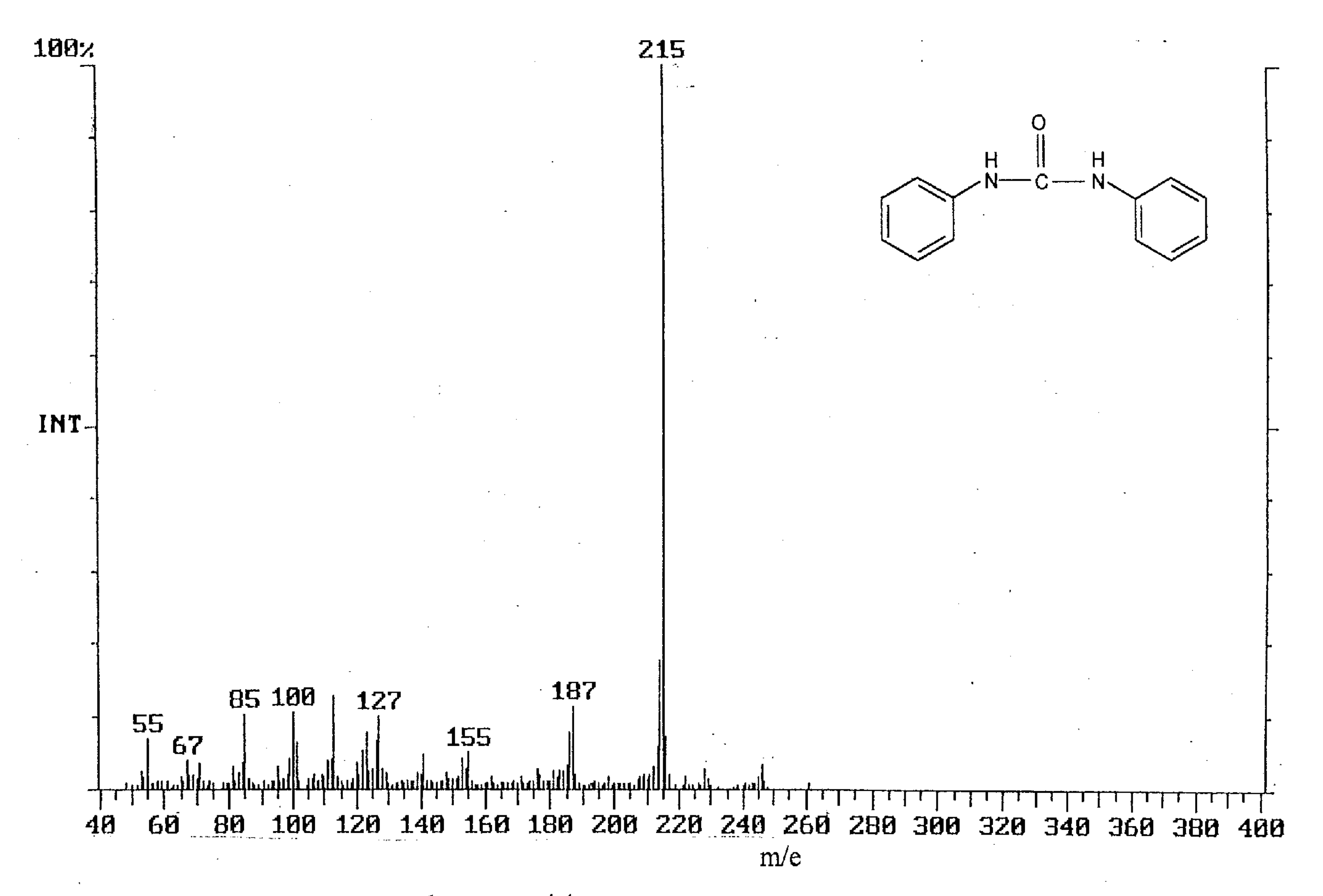


Figure 3.15: Mass spectrum of compound 4.

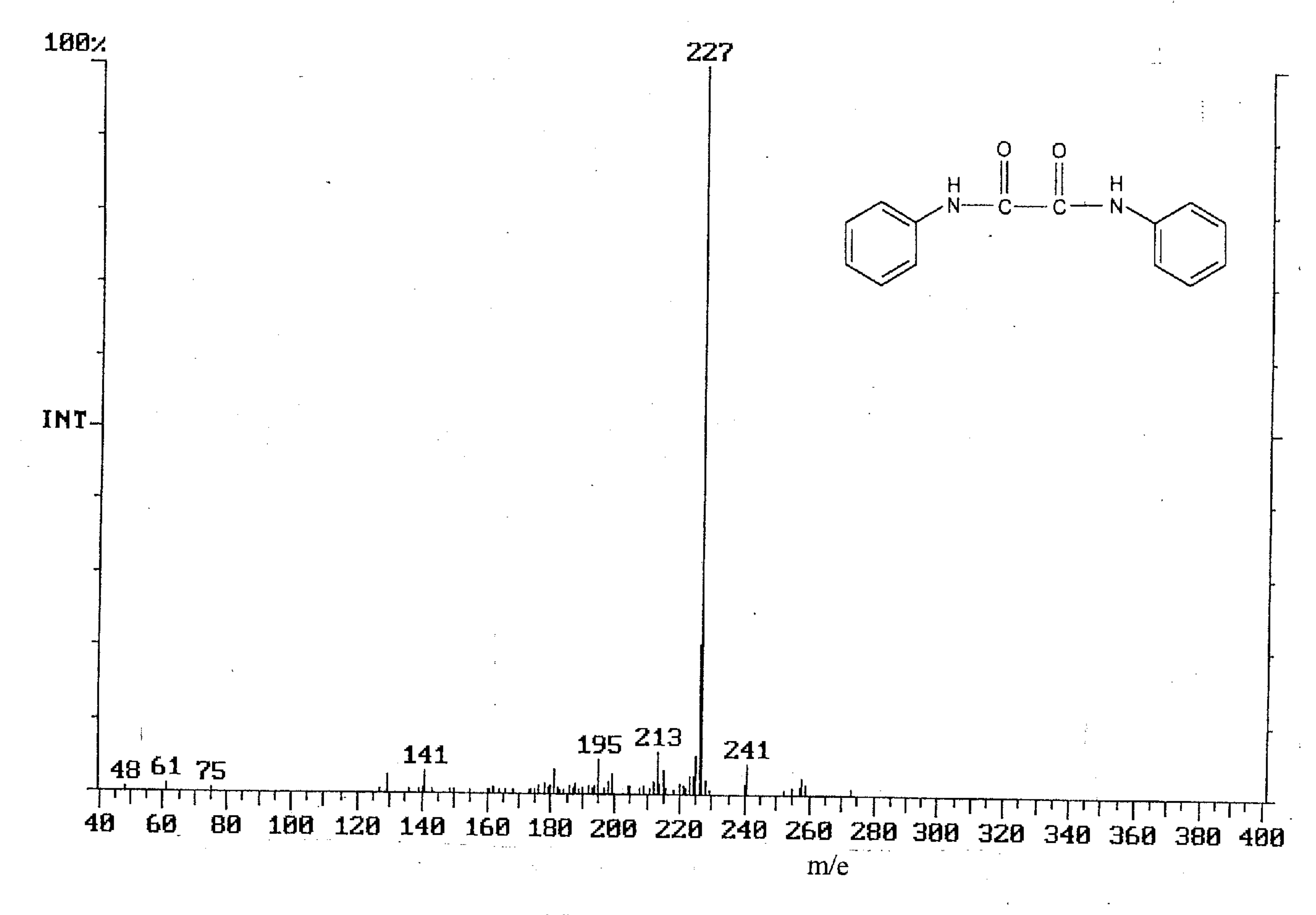


Figure 3.16: Mass spectrum of compound 5.

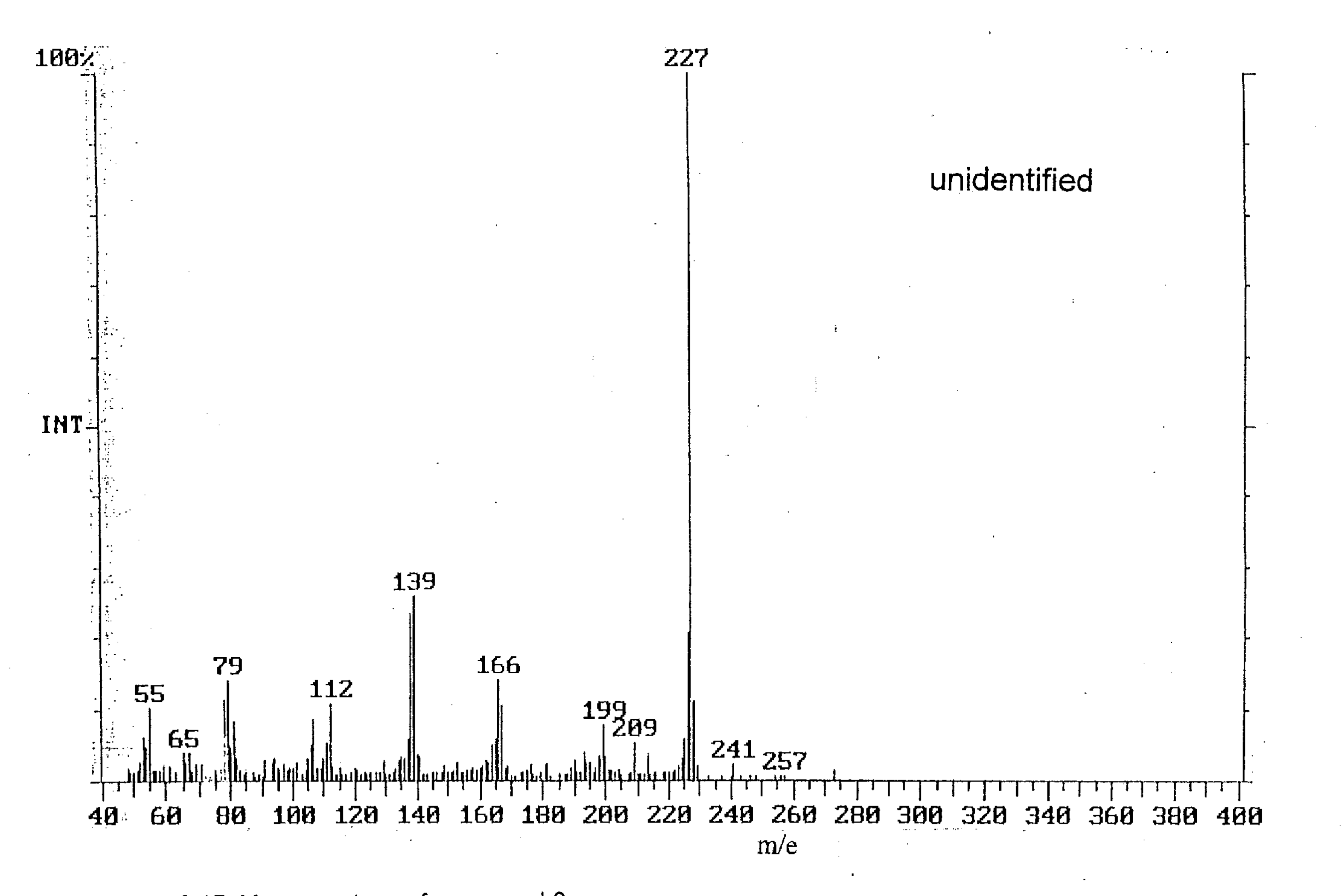


Figure 3.17: Mass spectrum of compound 6.

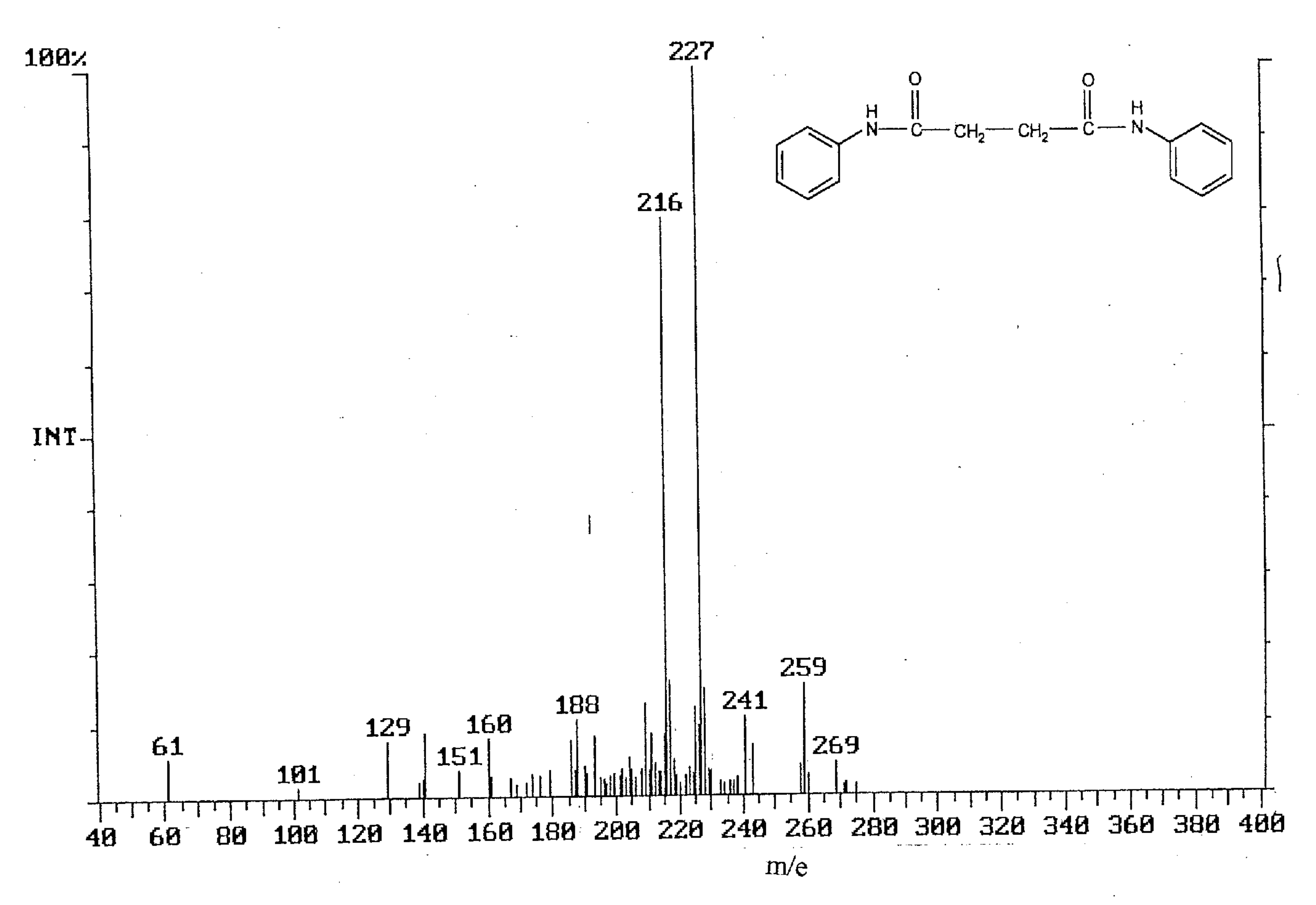


Figure 3.18: Mass spectrum of compound 7.

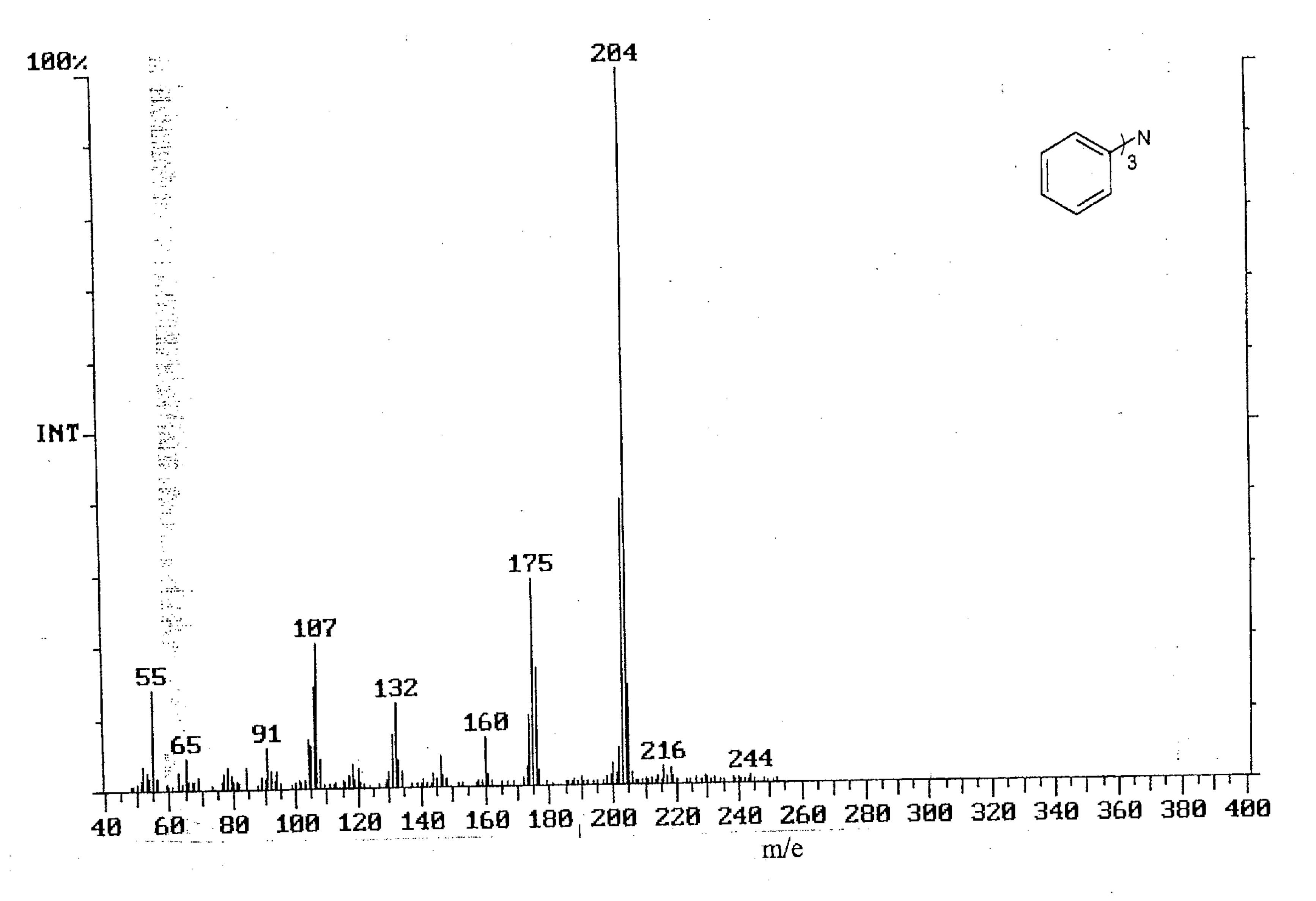


Figure 3.19: Mass spectrum of compound 8.

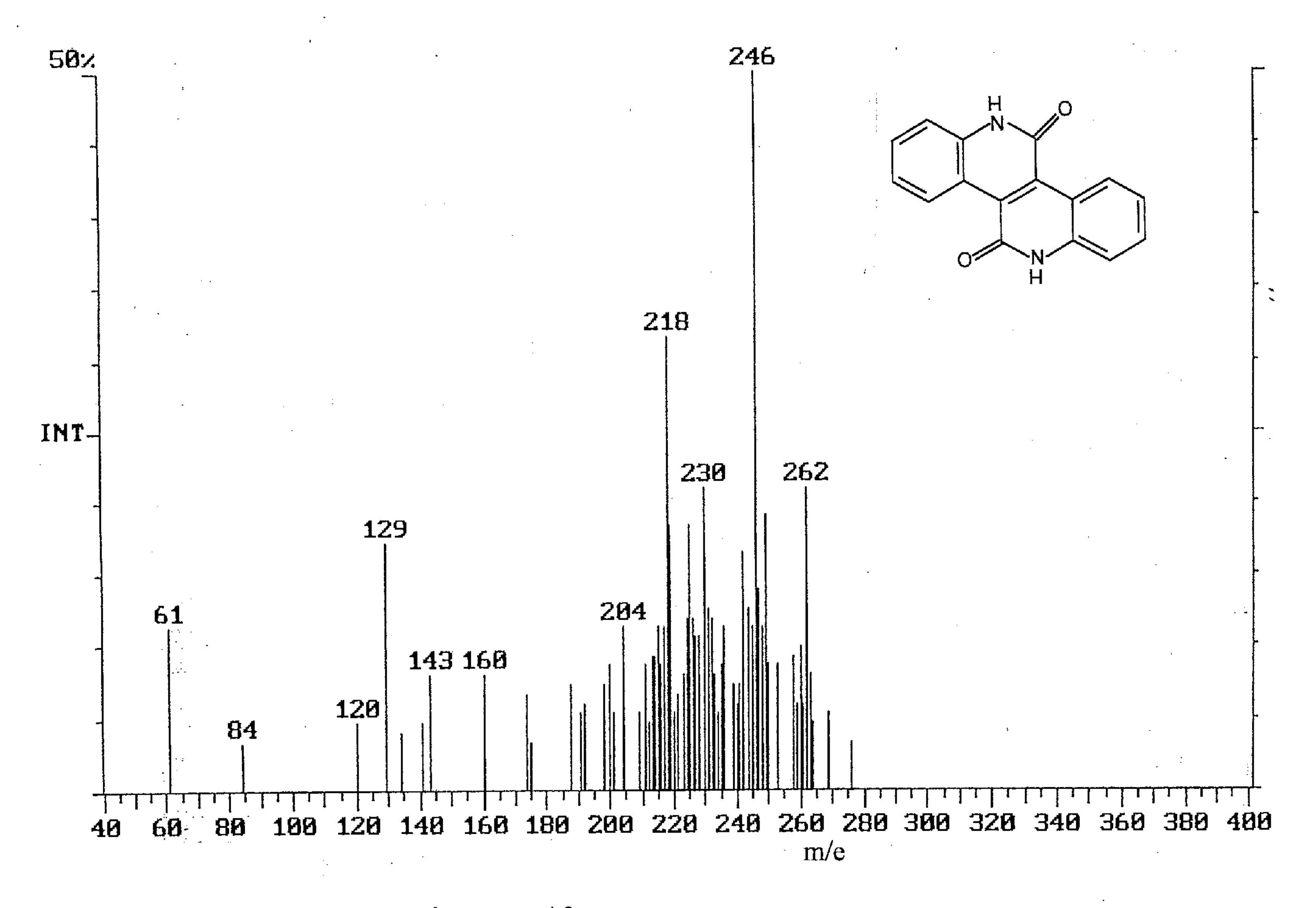


Figure 3.20: Mass spectrum of compound 9.

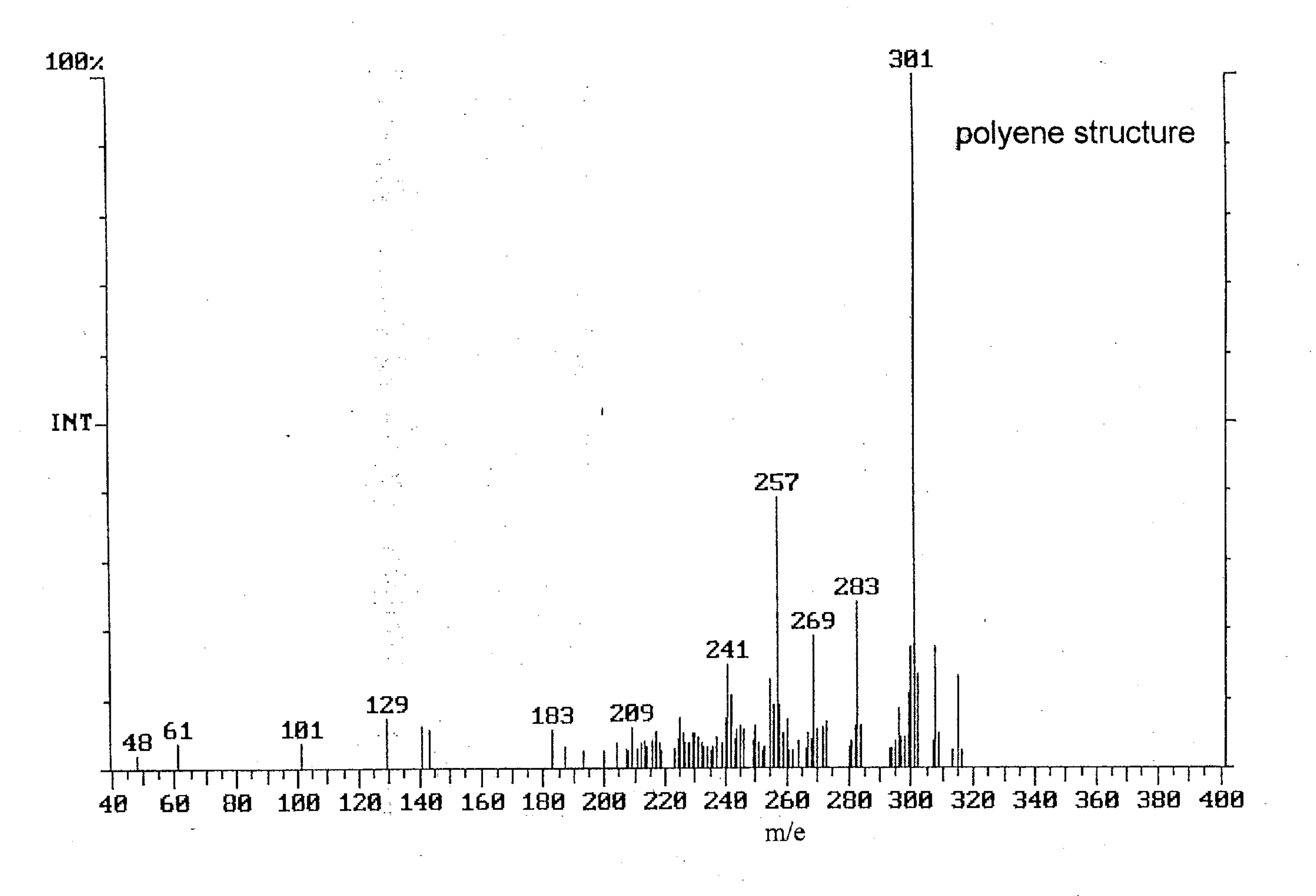


Figure 3.21: Mass spectrum of compound 10.

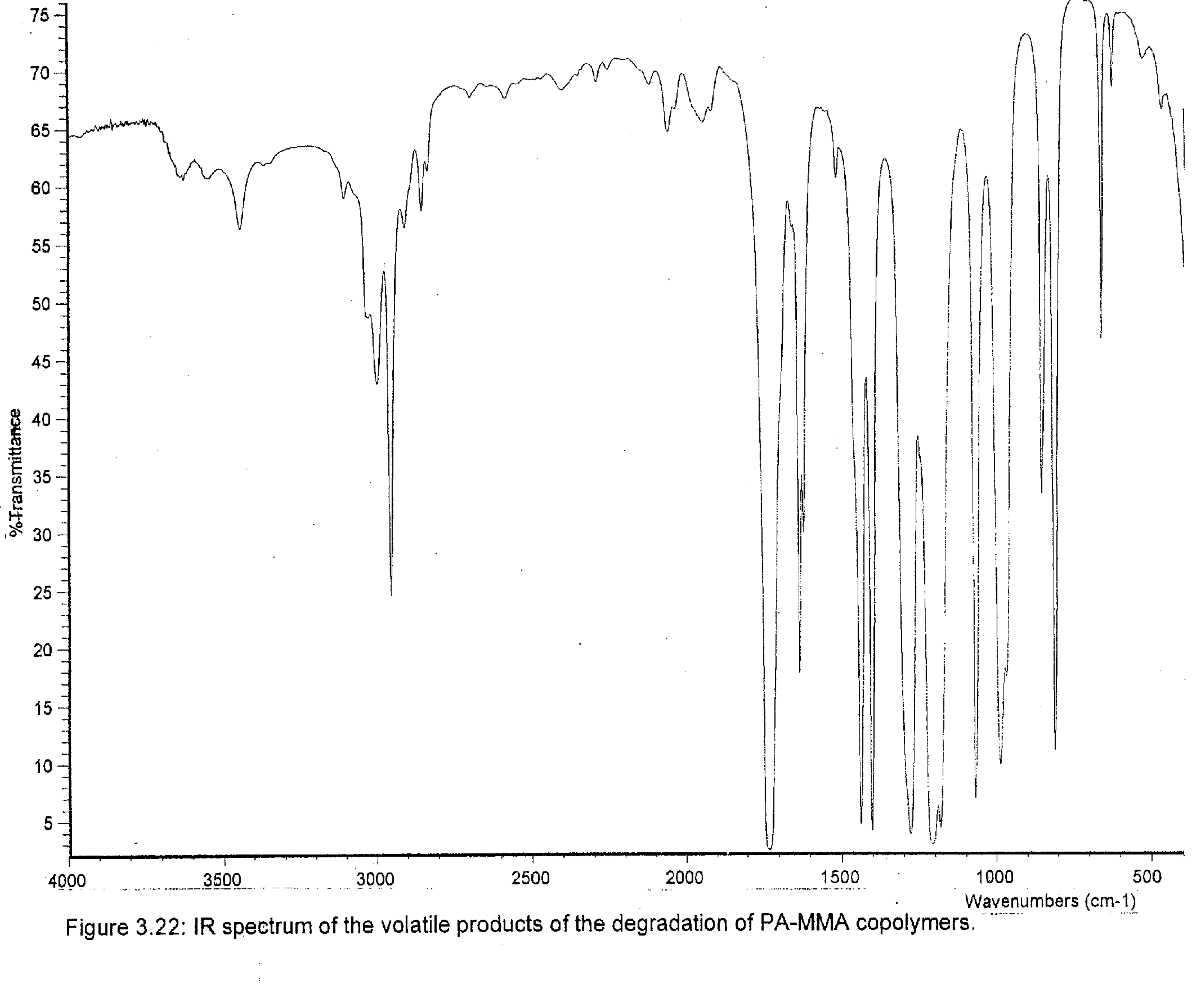


Figure 3.22: IR spectrum of the volatile products of the degradation of PA-MMA copolymers.

CHAPTER 4

POLY(p-TOLYL ACRYLAMIDE) HOMOPOLYMER AND COPOLYMERS OF p-TOLYL ACRYLAMIDE WITH METHYL METHACRYLATE

CHAPTER 4

POLY(p-TOLYL ACRYLAMIDE) HOMOPOLYMER AND COPOLYMERS OF p-TOLYL ACRYLAMIDE WITH METHYL METHACRYLATE

4.1. Introduction:

In Chapter 3, it was found that the stability of PPA homopolymer has been improved by copolymerization of PA with MMA monomer.

In this Chapter, homopolymer of p-tolyl acrylamide (PTA) and five different compositions of copolymers of p-tolyl acrylamide and methyl methacrylate (TA-MMA) have been prepared and the reactivity ratios of copolymerization were calculated. The thermal stabilities and degradation behaviours of the homopolymer and the copolymers were investigated. An interpretation of the mechanism of the degradation process is given.

4.2. Characterization of PTA homopolymer and TA-MMA copolymers:

p-Tolyl acrylamide (TA) monomer was prepared by the reaction of equimolar amounts of AC and p-toludine in dry benzene until the evolution of hydrogen chloride ceased forming a yellow powder of TA monomer. (M.W. 161). Microanalysis, found N, 9.1 %. Calcd. for $C_{10}H_{11}ON$, N, 8.7 %.

Homopolymer of PTA was prepared by free radical initiation of TA using 0.2 % w/v AIBN as initiator to about 10 % conversion. The IR spectrum of PTA homopolymer as shown in Figure 4.1 exhibits two broad bands at 3230 and 3440 cm^{-1} assigned to symmetric and asymmetric stretching vibrations of the amino group[144]. The band at 1680 cm^{-1} is due to the antisymmetric stretching

vibration of the amidic carbonyl group of the homopolymer[145]. TA-MMA copolymers were prepared by free radical initiation using 0.2 % w/v AIBN and DMF (50/50 v/v) as solvent. The IR spectrum of the copolymer (Figure 4.2) shows a characteristic strong band at 1730 cm^{-1} assigned to the antisymmetric stretching vibration of the carbonyl group of MMA in the copolymer[146]. The characteristic bands due to the amino and amidic carbonyl groups are also present in the IR spectrum of the copolymer.

4.3. Determination of reactivity ratios of TA-MMA copolymers:

Five different composition of the TA-MMA copolymers with 52, 31, 22, 16 and 13 mole % of TA units were prepared to about 5 % conversion. Figure 4.3 shows the ^{1}H-NMR spectrum of TA-MMA copolymers. The bands at δ 0.85-1.05, 1.88-1.94, 2.33 and 2.77-2.89 ppm are due to CH_3, CH_2 and CH protons of MMA and CH_3 and CH protons of TA units in the copolymers[146]. The band at δ 7.89 ppm is due to the amino proton was disappeared on addition of D_2O. Peak A in Figure 4.3 at δ 6.9 - 6.97 and 7.30 -7.38 ppm is a composite peak, due to two protons in the orth-position and two protons in the meta-position of the benzene ring of the TA unit in the copolymers, respectively. Peak B at δ 3.60 ppm is due to $-CH_3$ protons of the MMA unit in the copolymers. Dividing the integration values of peaks A and B by four and three, respectively, the monomer composition of the copolymer can be calculated. By knowing the number of moles of the monomer mixture and the molar ratio of the copolymer, reactivity ratio values can be calculated by applying the following equation[141].

$$\frac{f_1(1-2F_1)}{(1-f_1)\,F_1} = \frac{f_1^2(F_1-1)}{(1-f_1)^2F_1}\; r_1 \; + \; r_2$$

Where $F_1 = \frac{M_1/M_2}{M_1/M_2 + 1}$ is the mole fraction of TA (M_1) in copolymer, $f_1 = \frac{n_1}{n_1 + n_2}$ is

the mole fraction of M_1 in feed and r_1 and r_2 are the reactivity ratios of TA and

MMA, respectively. Figure 4.4 is a plot of $\frac{f_1^2 (F_1-1)}{(1-f_1)^2 F_1}$ versus $\frac{f_1 (1-2F_1)}{(1-f_1) F_1}$ and

Figure 4.5 is a plot of $\frac{f_2^2 (F_2-1)}{(1-f_2)^2 F_2}$ versus $\frac{f_2(1-2F_2)}{(1-f_2) F_2}$ where $F_2 = \frac{M_2/M_1}{M_2/M_1 + 1}$

is the mole fraction of MMA(M_2) in copolymer and $f_2 = \frac{n_2}{n_1 + n_2}$ is the mole

fraction of M_2 in feed. From the slopes and intercepts in Figures 4.4 and 4.5, reactivily ratio values for TA-MMA copolymers are r_1 (TA) = 1.4 ± 0.1 and r_2 (MMA) = 2.8 ± 0.1

4.4. <u>Thermal methods of analysis</u>:

4.4.1. <u>Thermogravimetry</u>:

TG curves of PTA and PMMA homopolymers and copolymers of TA-MMA are shown Figure 4.6. PTA homopolymer degrades in two stages. The first starts at ~ 112°C with a weight loss ~ 47 %. The second stage starts at ~ 319°C with a weight loss of ~ 44 %. PMMA homopolymer degrades in two stages. The first stage at ~ 260°C with a weight loss percentage of ~ 38 %. The second degradation stage starts at ~ 350°C with a weight loss of ~ 56%. There are three TG degradation stages for all the TA-MMA copolymers. The degradation temperatures started at ~ 130, 150, 190, 220 and 235°C for the copolymers 52, 31, 22, 16 and 13 mole % TA units, respectively. Table 4.1 lists the percentage weight losses and the maximum rate of weight loss shown by the derivative TG apparatus. TG curves reveal that the stability of the copolymers is intermediate between the two homopolymers. This is similar to the results obtained by Diab et al[58,134] with copolymers of 4-vinylpyridine and β-

bromostyrene with methyl methacrylate. The change in stability with composition is shown in Figure 4.7, in which the weight loss percentage at a selected temperature of 270°C in the programmed degradation TG using the data in Figure 4.6 is plotted against composition. Again it seems that the stability of the copolymers increases towards PMMA homopolymer.

The effective activation energies of the thermal degradation of PTA and PMMA homopolymers and TA-MMA copolymers were determined from the temperature dependence of the initial rate of degradation. Arrhenius plots are shown in Figure 4.8, from which values of activation energy decreasing from 116.4 to 43.6 KJ/mole were obtained as the TA concentration in the copolymers increase (Table 4.2). It is clear that the activation energies are in the same order as the stabilities.

4.4.2. Differential scanning calorimetry (DSC):

Glass transition temperatures (Tg) of PTA and PMMA homopolymers and TA-MMA copolymers were determined using DSC apparatus. Figure 4.9 shows the DSC curve of 31, 22 and 16 mole % unit of TA in TA-MMA copolymers. The Tg values of the homopolymers and copolymers in Table 4.3 indicate that these values increase with increasing the mole percentage of MMA in the copolymers.

4.4.3. Thermal degradation of PTA homopolymer and TA-MMA copolymers:

50 mg of PTA homopolymer was heated under vacuum from ambient temperature to 500°C. The volatile product of degradation was identified by IR specroscopy as shown in Figure 4.10. The bands at 3190, 3360 and 3430 cm^{-1} are due to symmetric and asymmetric stretching vibrations of p-toludine[142]. Also, the IR of the degradation gas products of PTA homopolymer show the existence of toluene and ammonia confirmed by the bands at 1490 and 2150

cm^{-1}, respectively. The degradation liquid products were subjected to the GC-MS under programmed heating condition from 40 to 200°C. Figure 4.11 shows the gas chromatogram of the liquid degradation products the PTA homopolymer to 500°C. Table 4.4 represents the degradation products which were identified by mass spectroscopic apparatus. Some of the peak could not be identified because of their small size or due to the unclear mass spectra. The numerous degradation products of PTA homopolymer indicate that the thermal break down occurs mainly in the C-N and carbonyl C-C bonds forming low-molecular-weight radicals such as:

I II III

IV V

VI

Combination of the formed radicals with a random scission mechanism along the backbone chain following the formation of these radicals can be the main source of the numerous degradation products.

Toluene, p-toludine and ammonia as major degradation products were formed by substraction of radicals with $H^{\bullet}$ which were confirmed by IR spectroscopy.

Figure 4.12 shows the mass spectrum of compound 1 listed in Table 4.4. It seems to be TA monomer in a trace amount. The mechanism of formation of TA monomer is similar to the one suggested by Grassie[143] in the thermal degradation of PMMA either by random scission or by initiation at an unsaturated chain end

Compound 1

m/e=162

Compound 2 (Figure 4.13) could be formed by dimerization reaction of radical III as follows:

2 III ⟶ Compound 2 m/e=214

The ,mass spectrum of the degradation product 3 as shown in Figure 4.14 is a termination reaction of the radicals II and IV:

II + IV ⟶ Compound 3 m/e=227

Figure 4.15 shows the mass spectrum of the suggested compound 4. It seems that this compound was formed by a reaction of the radicals III and IV:

III + IV ⟶ Compound 4 m/e=242

Dimerization of the radical IV gives the assignment structure 5 as shown in Figure 4.16

IV

Compound 5
m/e=263

The assignment structure of compound 6 (Figure 4.17) is a reaction of TA monomer and the radical IV.

IV

Compound 6
m/e = 294

The mass spectrum of compound 7 (Figure 4.18) is a termination reaction between the radicals III and V followed by rearrangement giving the assignment structure 9.

III + V →

rearangment →

→

→

→

Compound 7

m/e=294

The assignment structure of compound 8 (Figure 4.19) suggesting the polyene structure. The major m/e fragments as shown in Table 4.4 decreasing by either 14 or 13 supporting the polyene structures. This is similar to the results obtained in the thermal degradation of polyolefines[31], which produced chain fragments between C_6-C_{60}.

The mass spectrum of compound 9 as shown in Figure 4.20. It seems that it was formed by a combination reaction between the radicals II and VI:

II + VI →

Compound 9
m/e=313

Again, the mass spectrum of compound 10 as shown in Figure 4.21 seems to be polyene structure derived from polyene radicals:

$$\text{~}\left(CH_2 - \dot{C}H - CH_2 - \dot{C}H\right)_n\text{~} \longrightarrow \text{~}\left(CH_2 - CH{=}CH - CH_2\right)_n\text{~}$$

Compound 11 (Figure 4.22) is TA dimer, and can be formed by a disproportionation process to form the dimer.

The assignment structure of compound 12 as shown in Figure 4.23 is a termination reaction between the radicals IV and VI:

IV + VI →

Compound 12
m/e = 368

The thermal degradation of TA-MMA copolymers has been studied in order to determine the nature and extent of any interaction which may occur between the comonomer units during the degradation. Figure 4.24 shows the IR spectrum of the volatile products of degradation of TA-MMA copolymers. Toluene, p-tolidine, ammonia and methyl methacrylate monomer are the main degradation gas products. GC-MS of the liquid fraction of the degradation of TA-MMA copolymers shows similar pattern as in the PTA homopolymer. It seems that there is no interaction between the comonomers in the degradation of copolymers.

Table 4.1: Weight loss percentage of PTA and PMMA homopolymers and TA-MMA copolymers

Polymer Mole%TA	Volatilization temperature, °C	First stage		Second stage		Third stage		Remaining Wt.% after 500°C
		T_{max}, °C	Wt.loss,%	T_{max}, °C	Wt.loss,%	T_{max}, °C	Wt.loss,%	
PTA	112	250	47	370	44	–	–	9
52	130	160	18	270	32	370	46	4
31	150	180	10	285	42	380	41	7
16	200	210	7	290	38	385	48	7
13	230	240	6	300	38	390	50	6
PMMA	260	297	38	350	56	–	–	6

Table 4.2: Activation energies of the thermal degradation of PTA and PMMA and PMMA homopolymers and TA-PMMA copolymers

Polymer TA mole %	Activation energy(Ea) KJ /mol
PTA	43.6
52	56.2
31	69.3
22	78.5
16	83.1
13	93.5
PMMA	116.4

Table 4.3: Glass transition temperature (Tg) of PTA and PMMA homopolymers and TA-PMMA copolymers

Polymer Mole % PA	Tg , °C
PTA	71
51	75
31	78
22	83
16	96
13	100
PMMA	111

Table 4.4: GC-MS data of the liquid fraction of the thermal degradation of PTA homopolymer to 500°C.

Compound No.	Retention Time, min.	Major MS fragments	Suggested Structure (Most probable)
1	10.73	162, 141,105,87,74, 61, 48	$CH_2{=}CH{-}C(=O){-}NH{-}C_6H_4{-}CH_3$
2	11.53	214, 187,162,141, 105,74, 61, 48	$H_3C{-}C_6H_4{-}NH{-}NH{-}C_6H_4{-}CH_3$
3	12.11	227,195,158,125,105, 78, 65,53	$H_3C{-}C_6H_4{-}C(=O){-}NH{-}C_6H_4{-}CH_3$

Cont'd: Table 4.4: GC-MS data of the liquid fraction of the thermal degradation of PTA homopolymer to 500°C.

Compound No.	Retention Time, min.	Major MS fragments	Suggested Structure (Most probable)
4	13.93	242,218,204,190,129, 104, 61,48	H_3C H N C O N H CH_3
5	14.58	269,259,237,227,216, 188,177, 160,141,105, 61, 48	H_3C H N C O C O N H CH_3
6	15.40	294,252,217,203,174, 160,146, 128,106,91, 65	CH_3 H N C O CH=CH C O N H CH_3

Cont'd: Table 4.4: GC-MS data of the liquid fraction of the thermal degradation of PTA homopolymer to 500°C.

Compound No.	Retention Time, min.	Major MS fragments	Suggested Structure (Most probable)
7	15.73	294,266,245,229,217,188,174, 144, 130,106,91, 63	
8	17.96	301,283,269,255,241,225,208, 199, 181,149,121,113,94,79,67,55	Polyene structure
9	18.30	313,295,280,265,248,220,203, 188, 172,160,144,133,106,91,79, 65,53	

Cont'd: Table 4.4: GC-MS data of the liquid fraction of the thermal degradation of PTA homopolymer to 500°C.

Compound No.	Retention Time, min.	Major MS fragments	Suggested Structure (Most probable)
10	18.41	313,295,280,265,234,220,192,161,133, 105,91, 77,55	Polyene structure
11	18.73	329, 310,280,264,247,235,221,204,188, 172,160,141,132,107,91,81,67,55	$H_2C—CH_2—C{=}CH_2$; O=C–NH; O=C–NH; CH_3; CH_3
12	19.18	368,294,281,269,257,248,237,220,202, 186,160,133,106,91,79,65	CH_3–C6H4–NH–C(=O)–NH–$(CH_2)_3$–C(=O)–NH–C6H4–CH_3

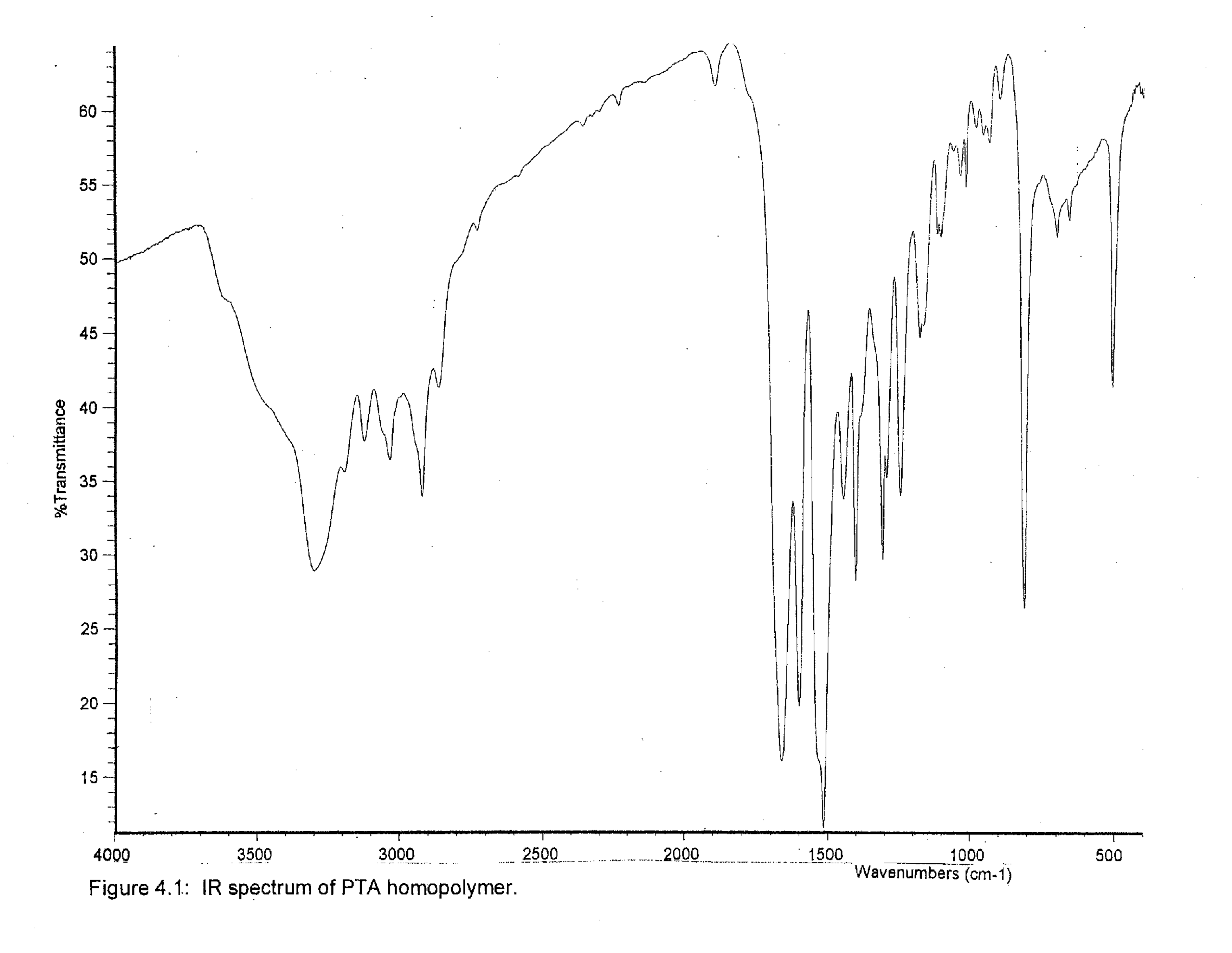


Figure 4.1: IR spectrum of PTA homopolymer.

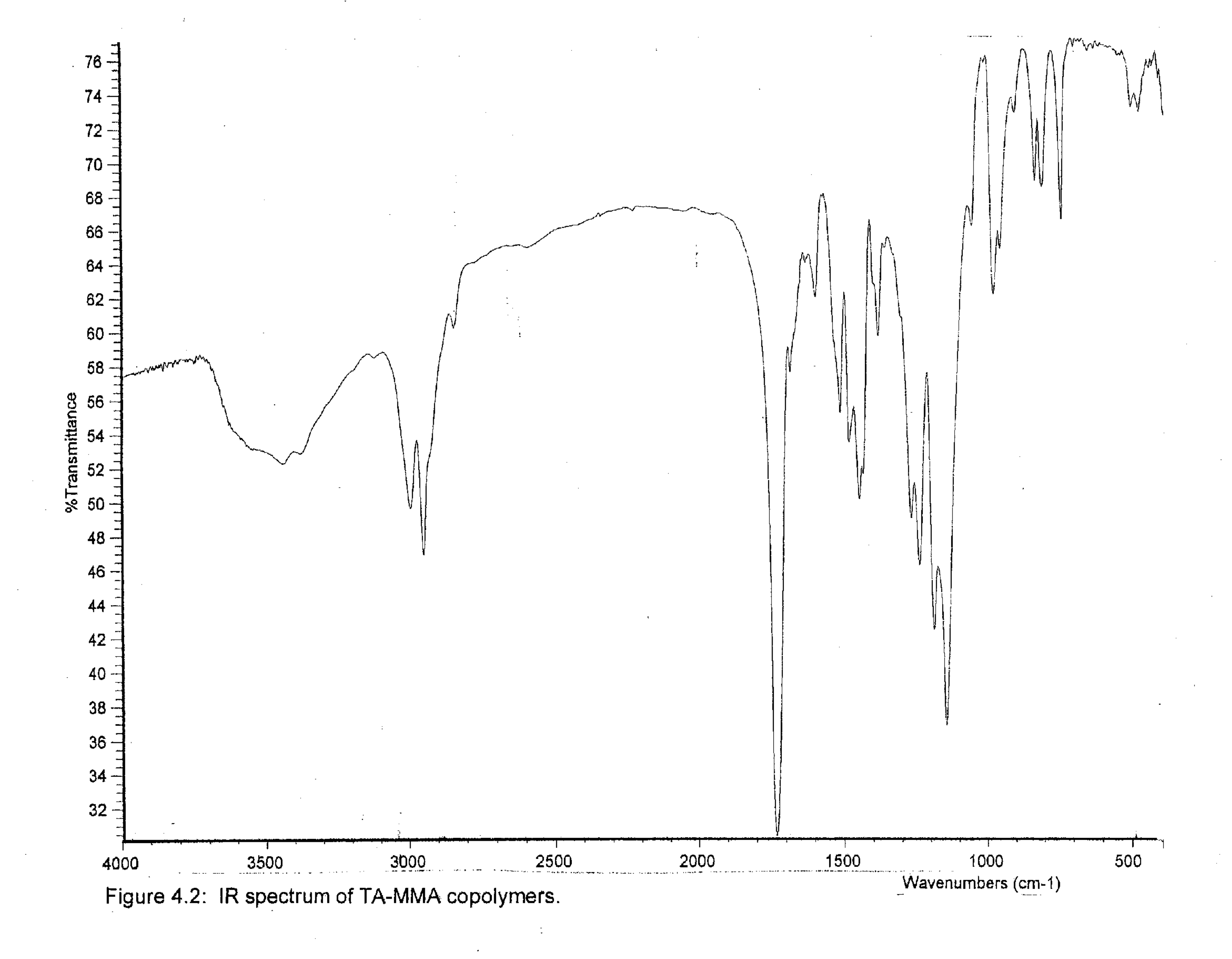


Figure 4.2: IR spectrum of TA-MMA copolymers.

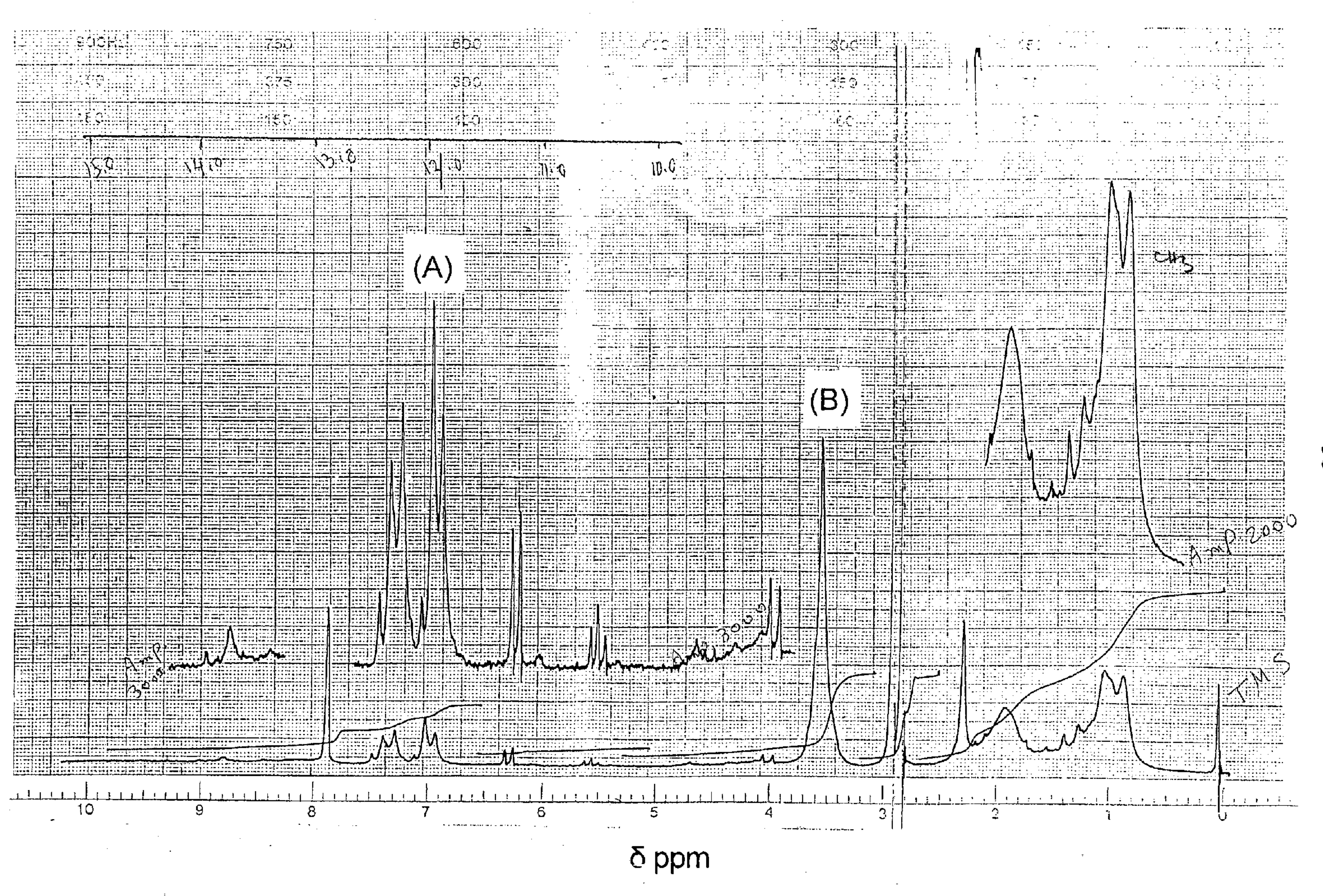


Figure 4.3: ^{1}H-NMR of TA-MMA copolymers.

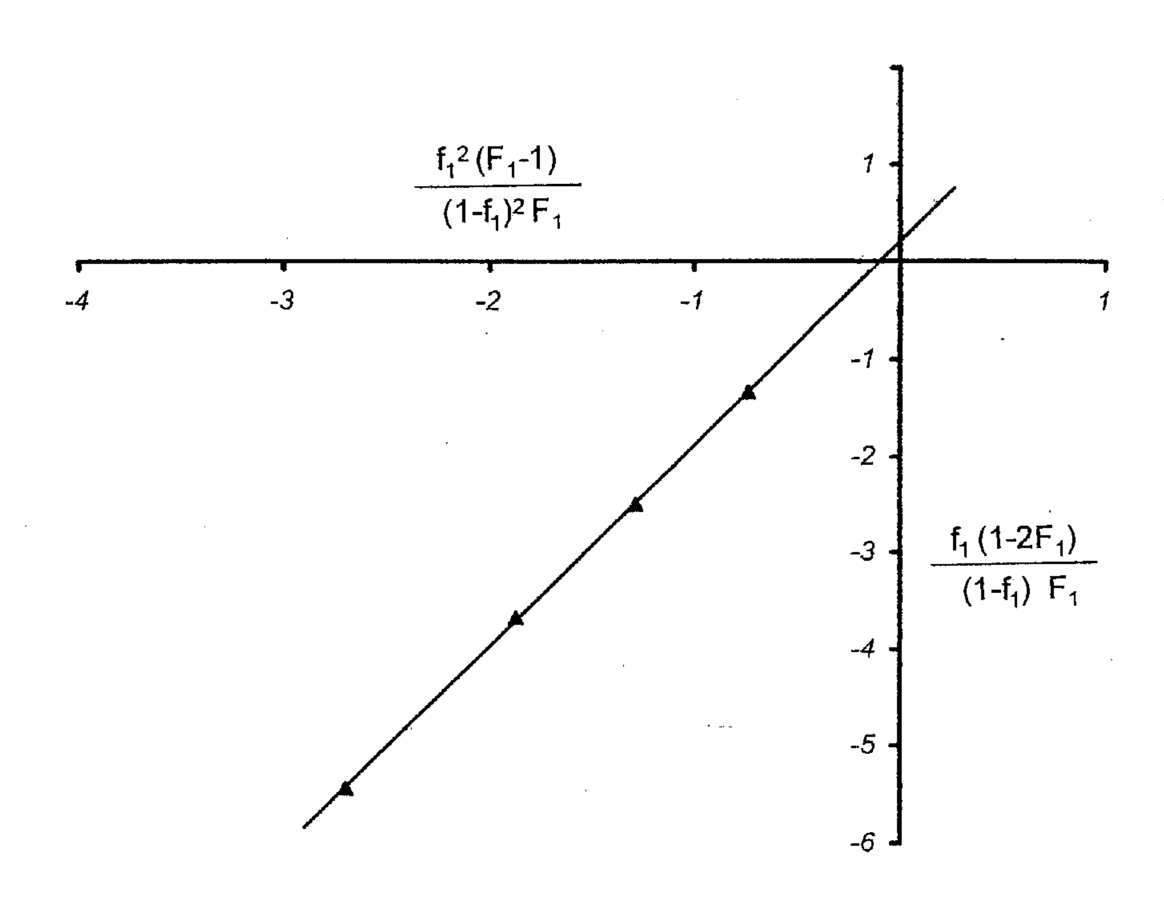


Figure 4.4: Graph of $\frac{f_1^2(F_1-1)}{(1-f_1)^2 F_1}$ versus $\frac{f_1(1-2F_1)}{(1-f_1)\ F_1}$ for TA-MMA copolymers.

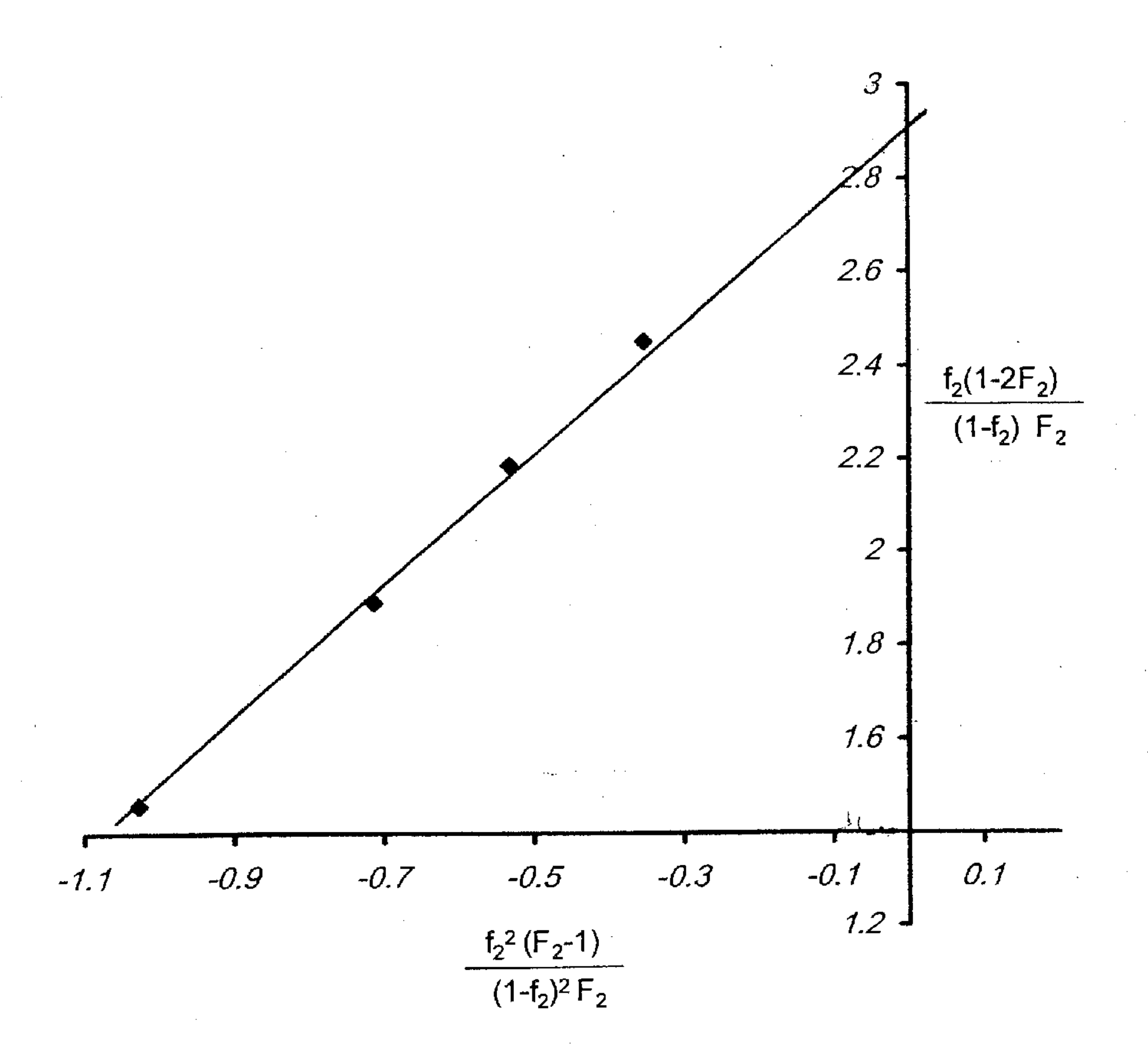


Figure 4.5: Graph of $\frac{f_2^2\,(F_2-1)}{(1-f_2)^2\,F_2}$ versus $\frac{f_2(1-2F_2)}{(1-f_2)\ F_2}$ for TA-MMA copolymers.

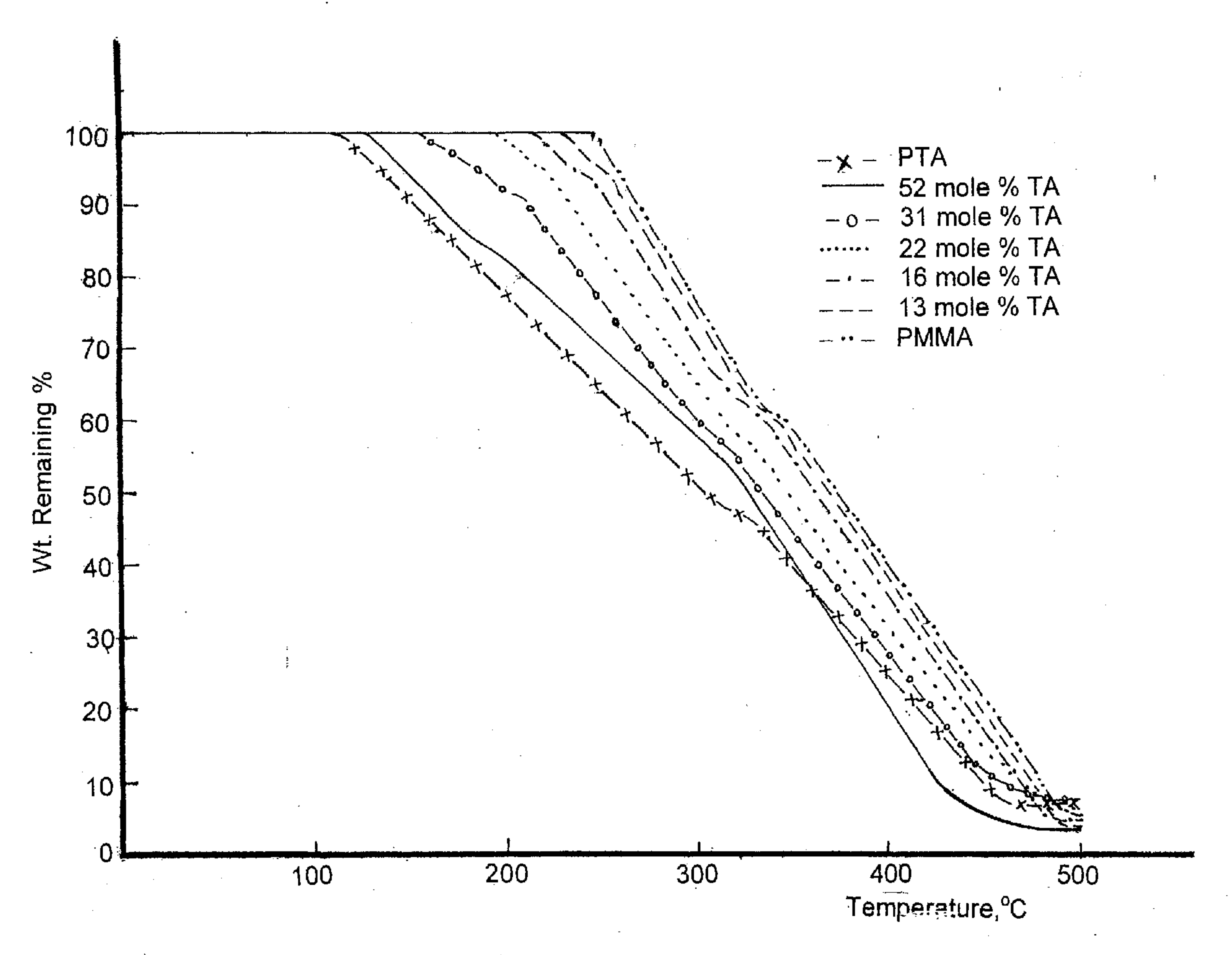


Figure 4.6: TG curves for PTA and PMMA homopolymers and TA-MMA copolymers.

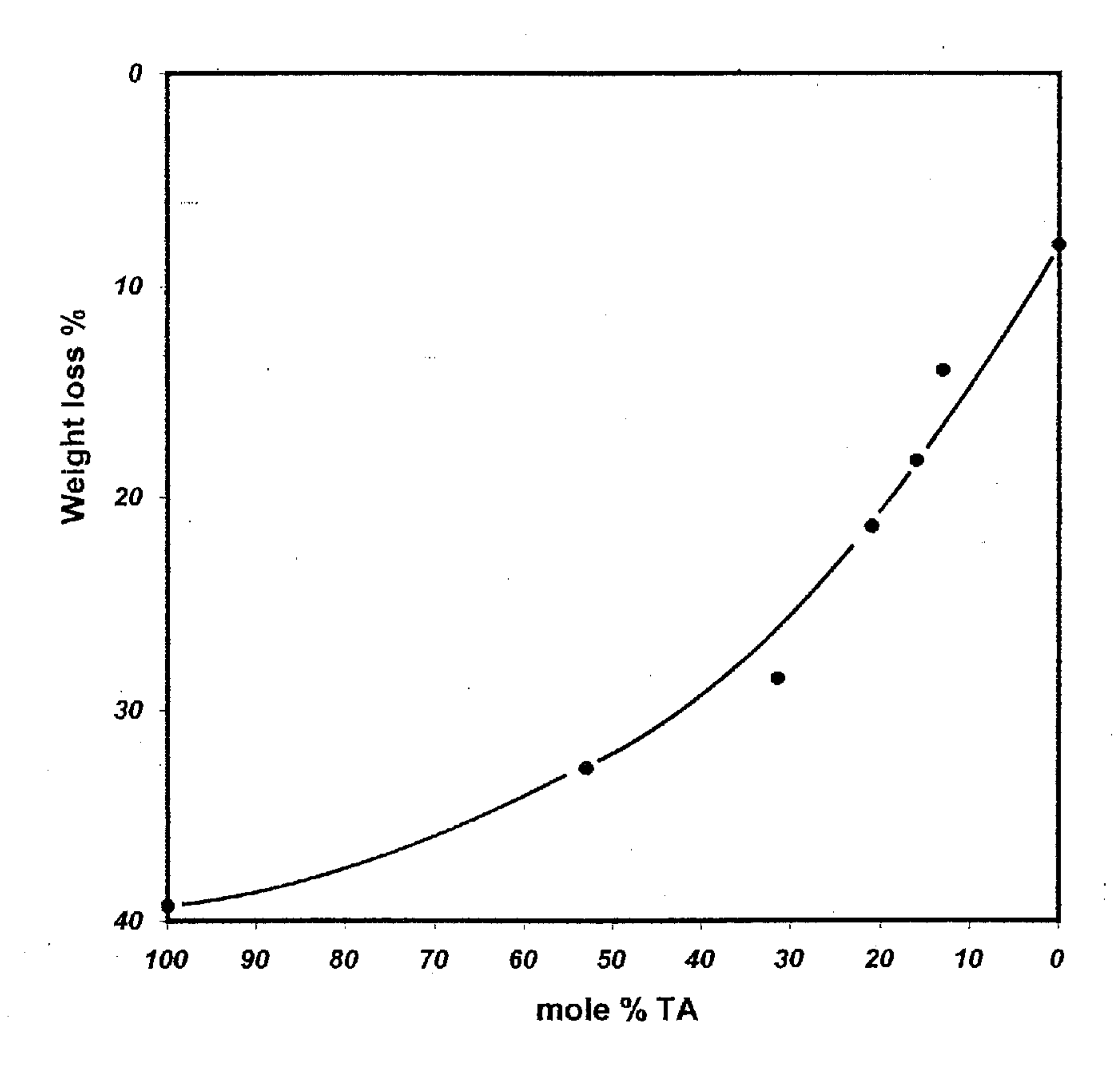


Figure 4.7: Comparison of weight loss percentage at 270 °C for TA-MMA copolymers at different compositions.

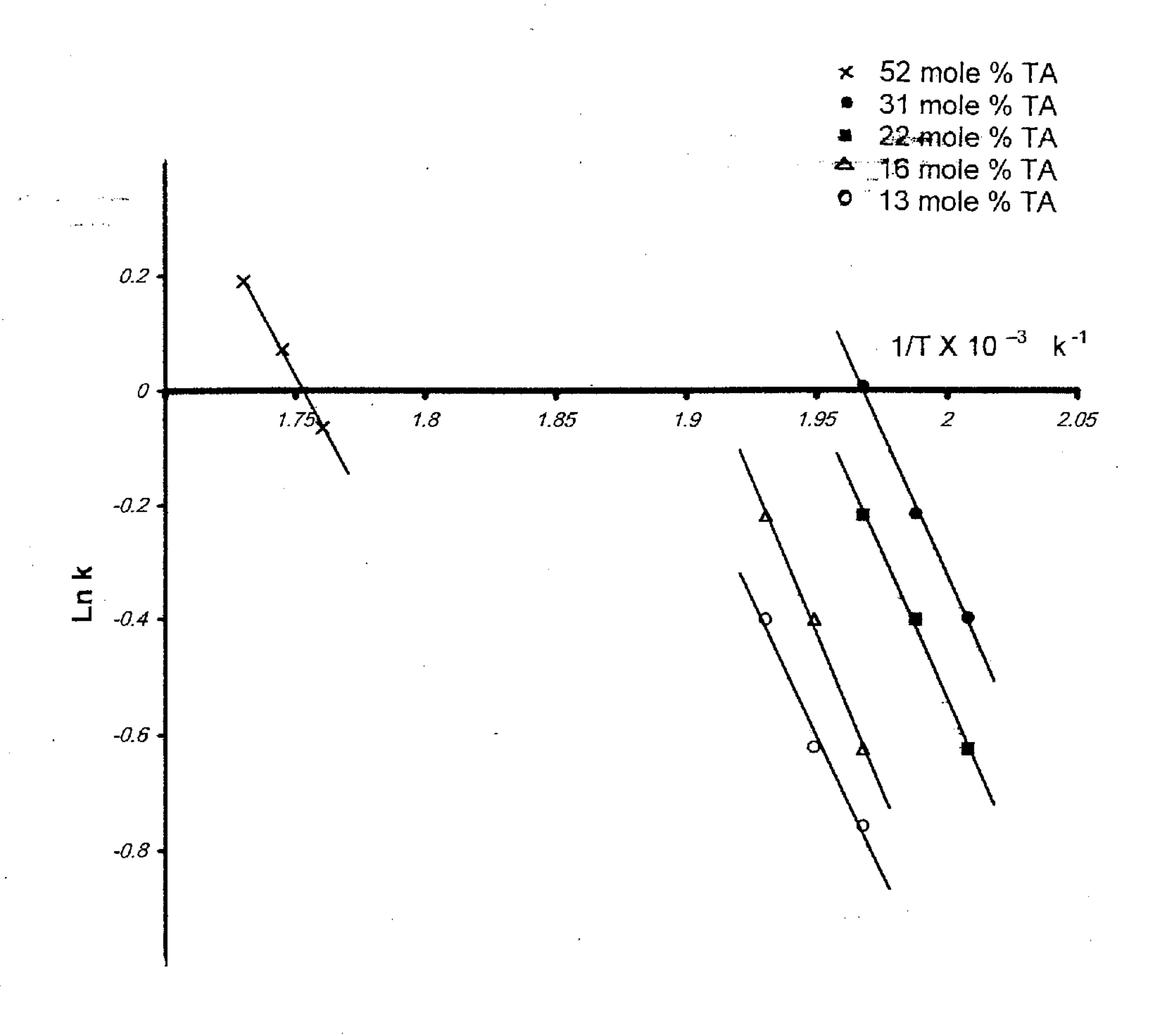


Figure 4.8: Arrhenius plots of the rate constants of degradation of TA-MMA copolymers.



60.00
80.00
100.0
120.0
140.0
Temp. °C
31 % mol

60.00
80.00
100.0
Temp. °C
22 % mol

100.0
200.0
300.0
400.0
500.0
Temp. °C
16 % mol

Figure 4.9: DSC curve of TA-MMA copolymers (31, 22 and 16 mol% TA).

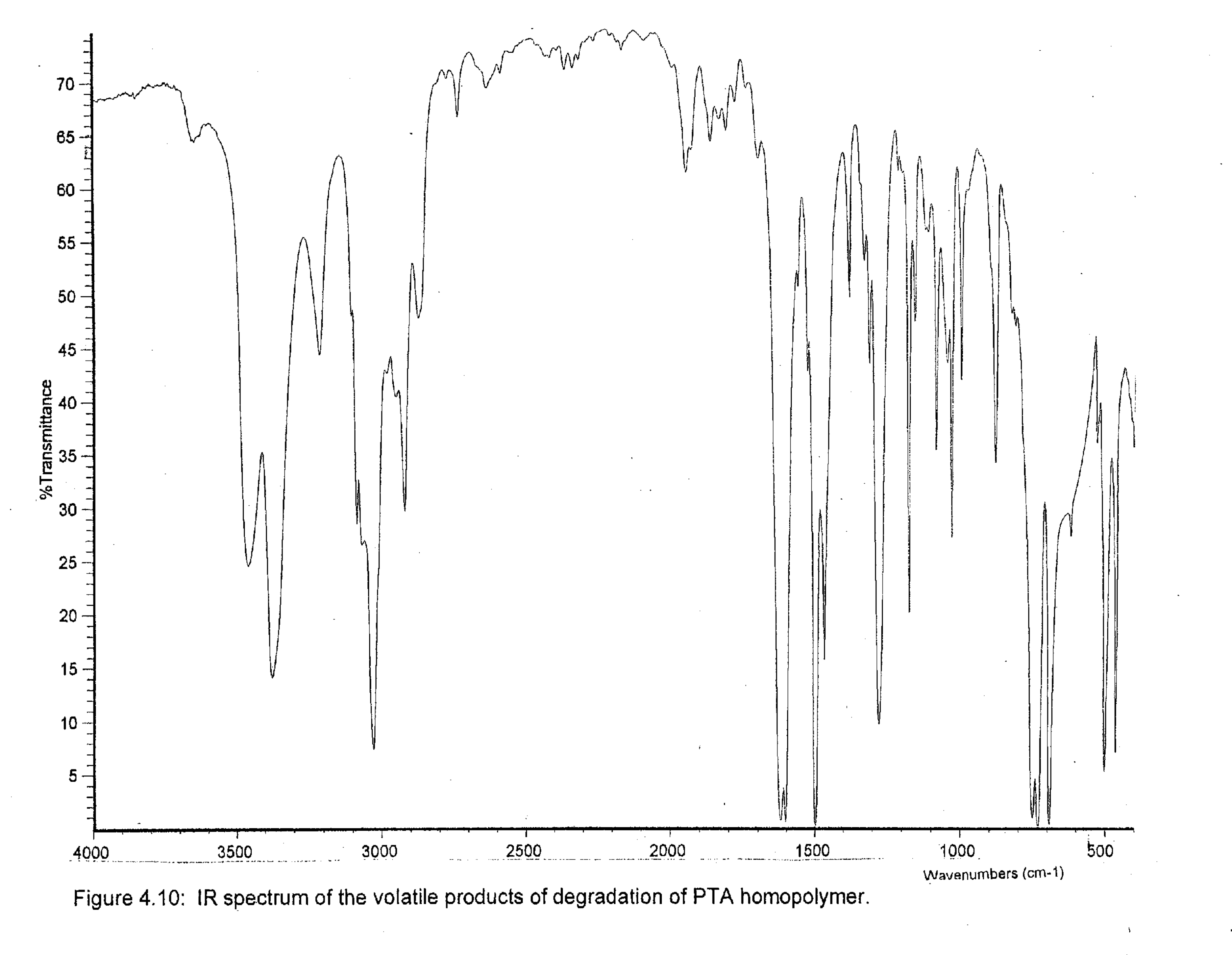


Figure 4.10: IR spectrum of the volatile products of degradation of PTA homopolymer.

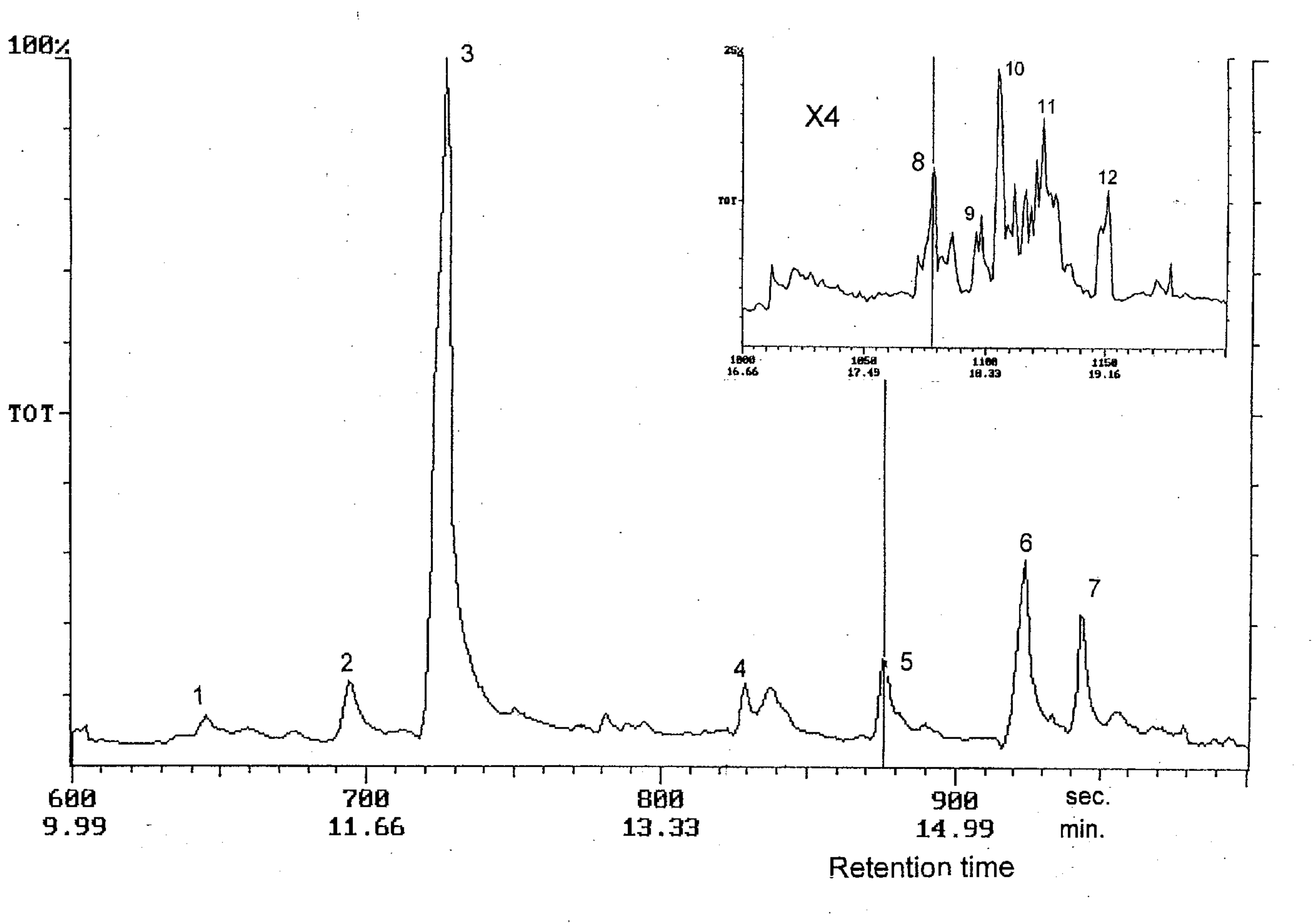


Figure 4.11: GC curves of the liquid fraction of thermal degradation of PTA homopolymer.

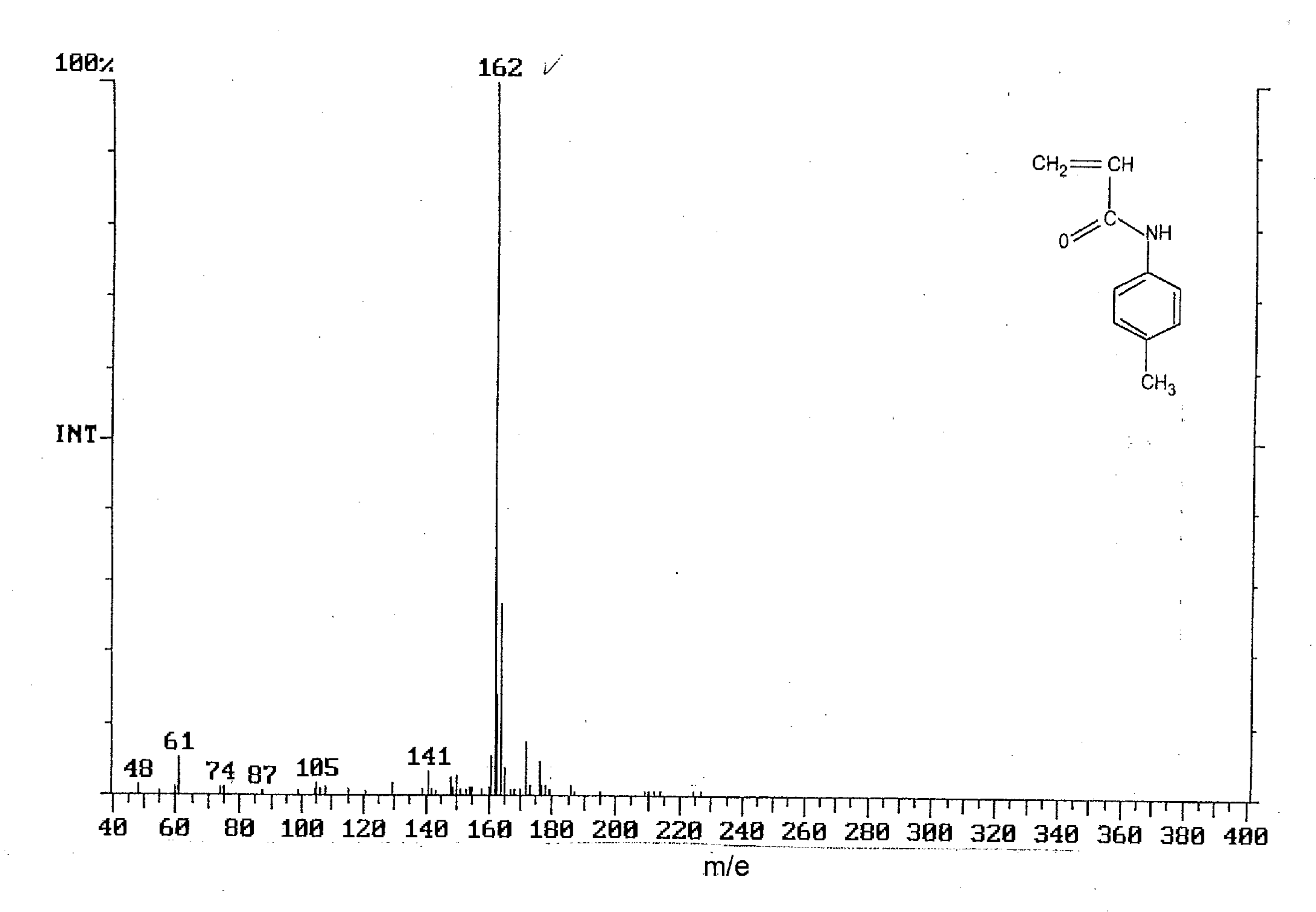


Figure 4.12: Mass spectrum of compound 1.

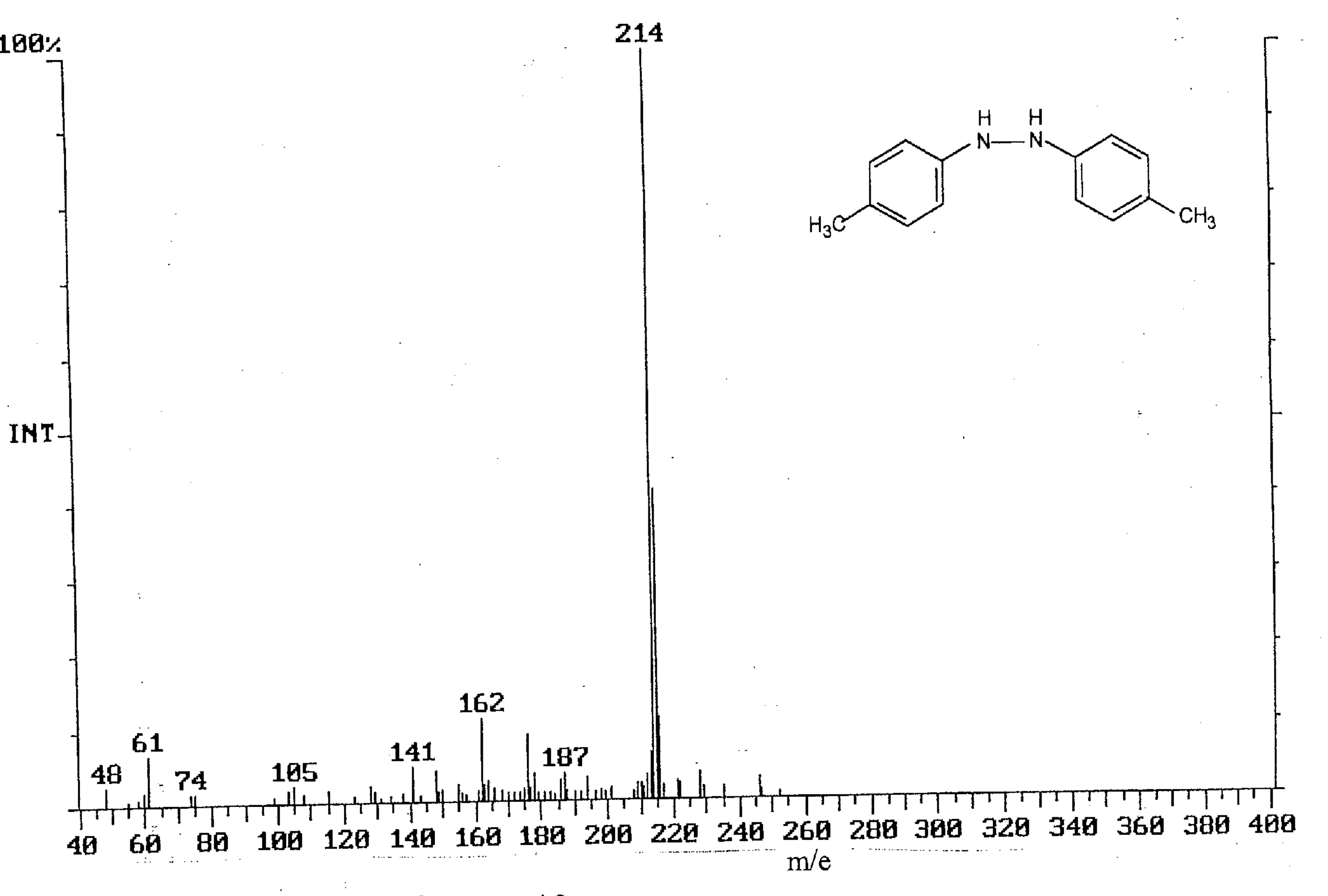


Figure 4.13: Mass spectrum of compound 2.

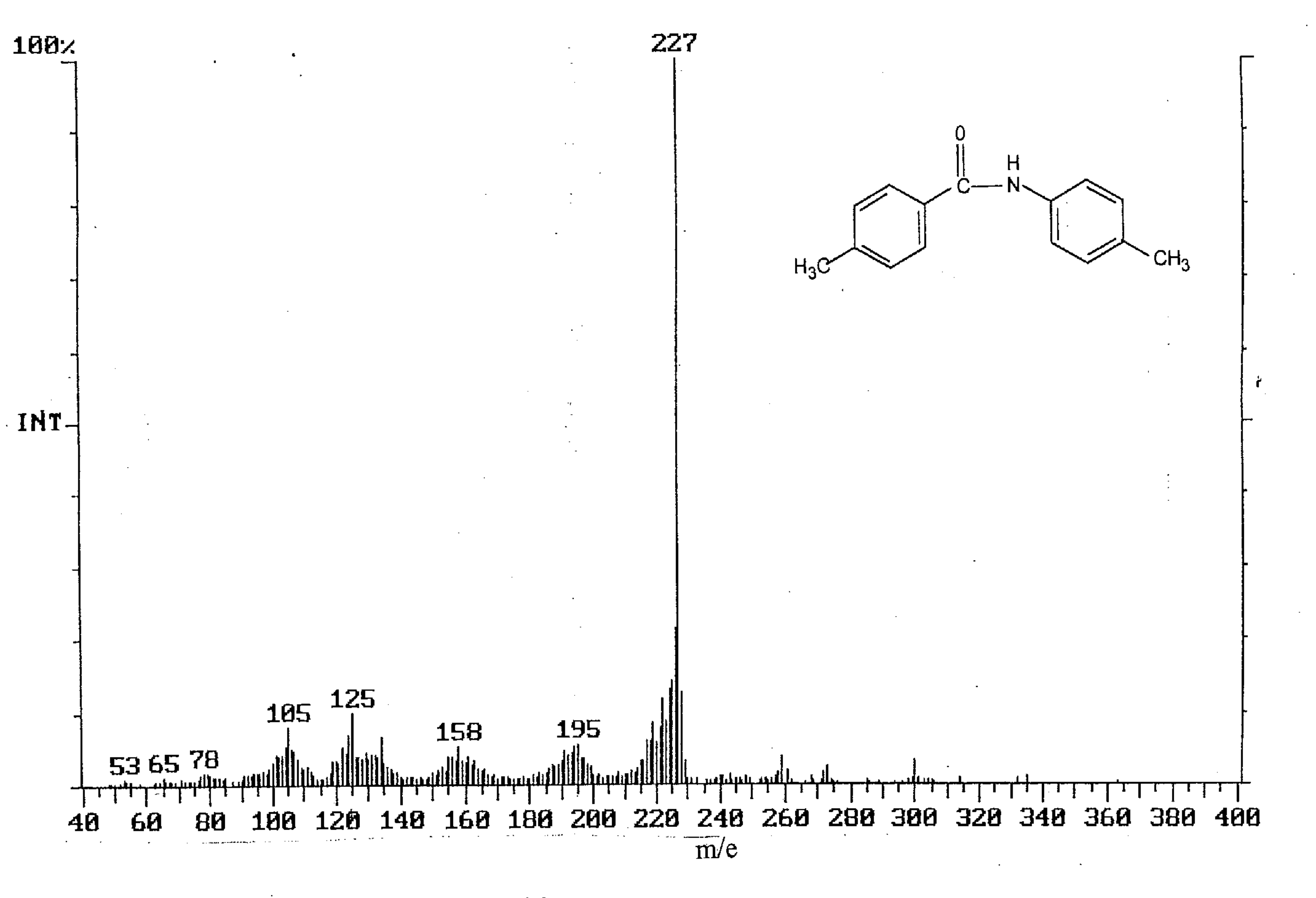


Figure 4.14: Mass spectrum of compound 3.

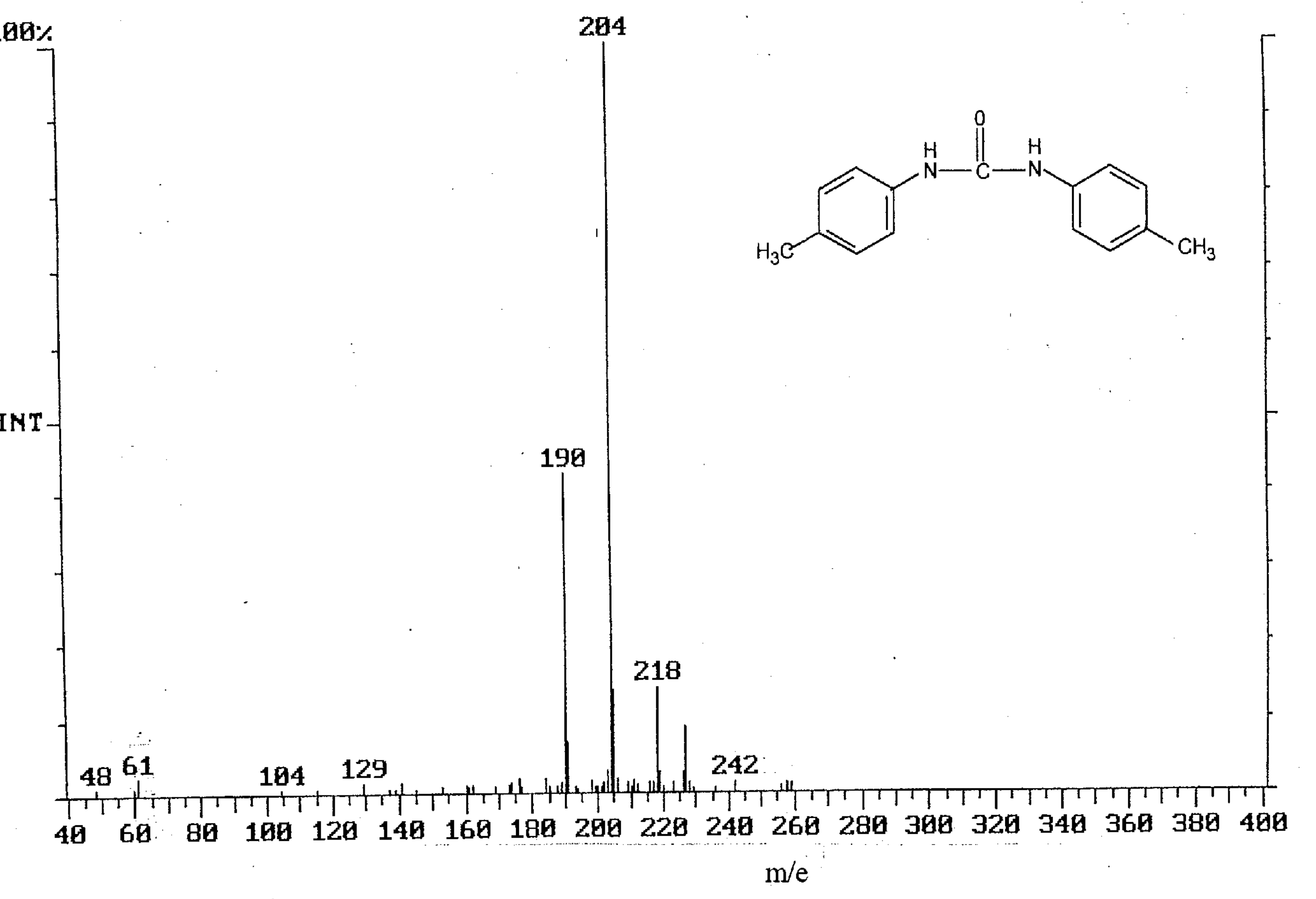


Figure 4.15: Mass spectrum of compound 4.

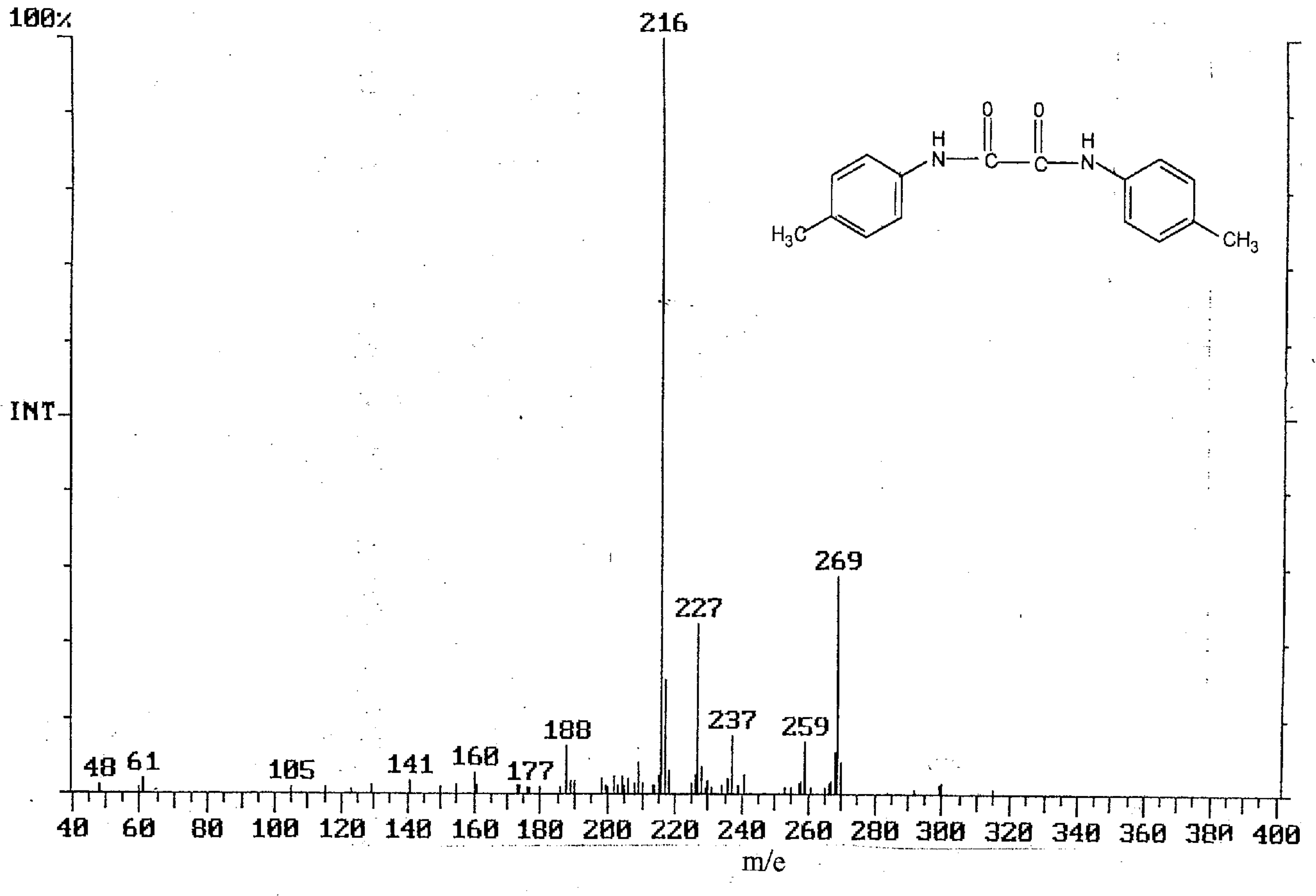


Figure 4.16: Mass spectrum of compound 5.

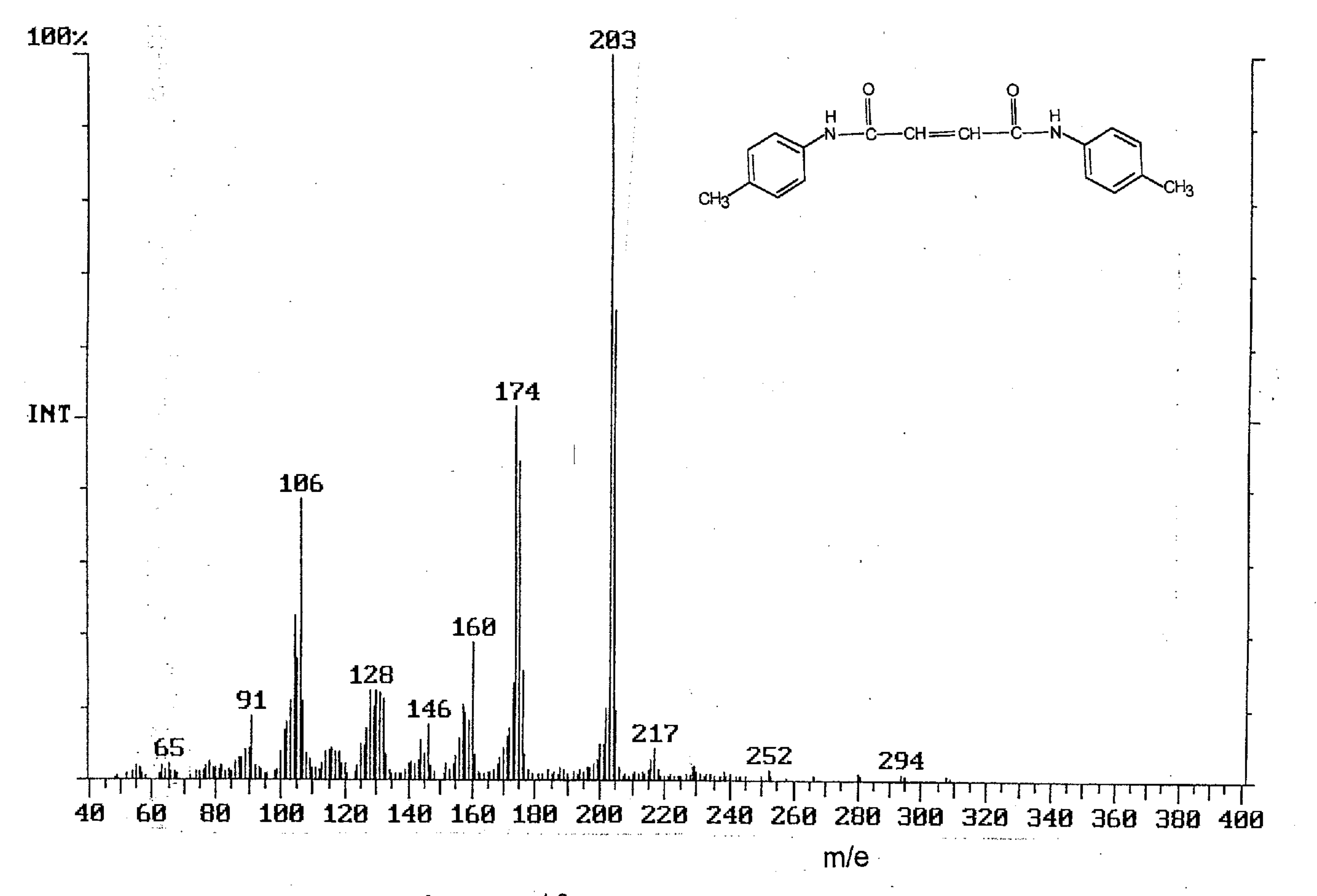


Figure 4.17: Mass spectrum of compound 6.

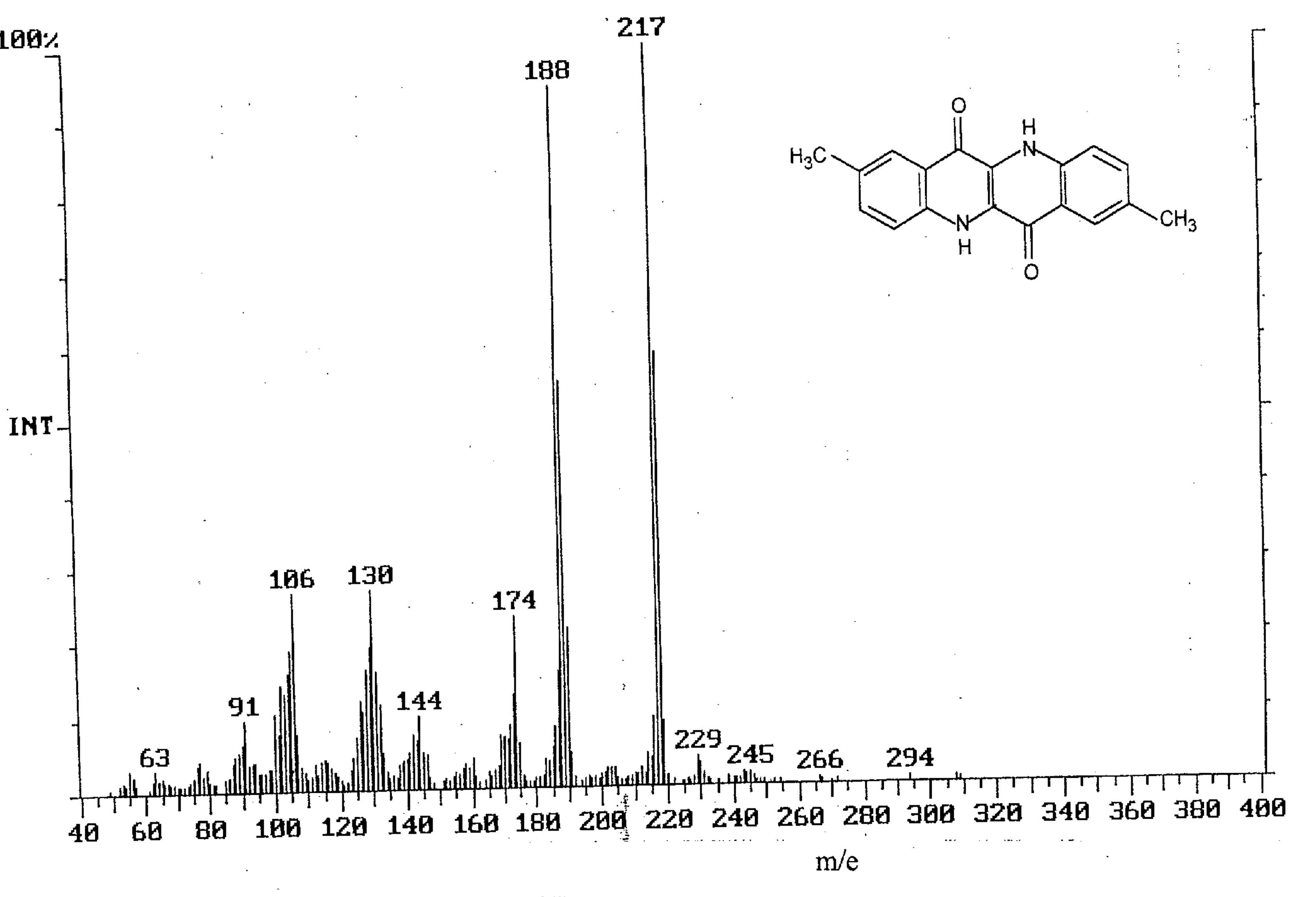


Figure 4.18: Mass spectrum of compound 7.

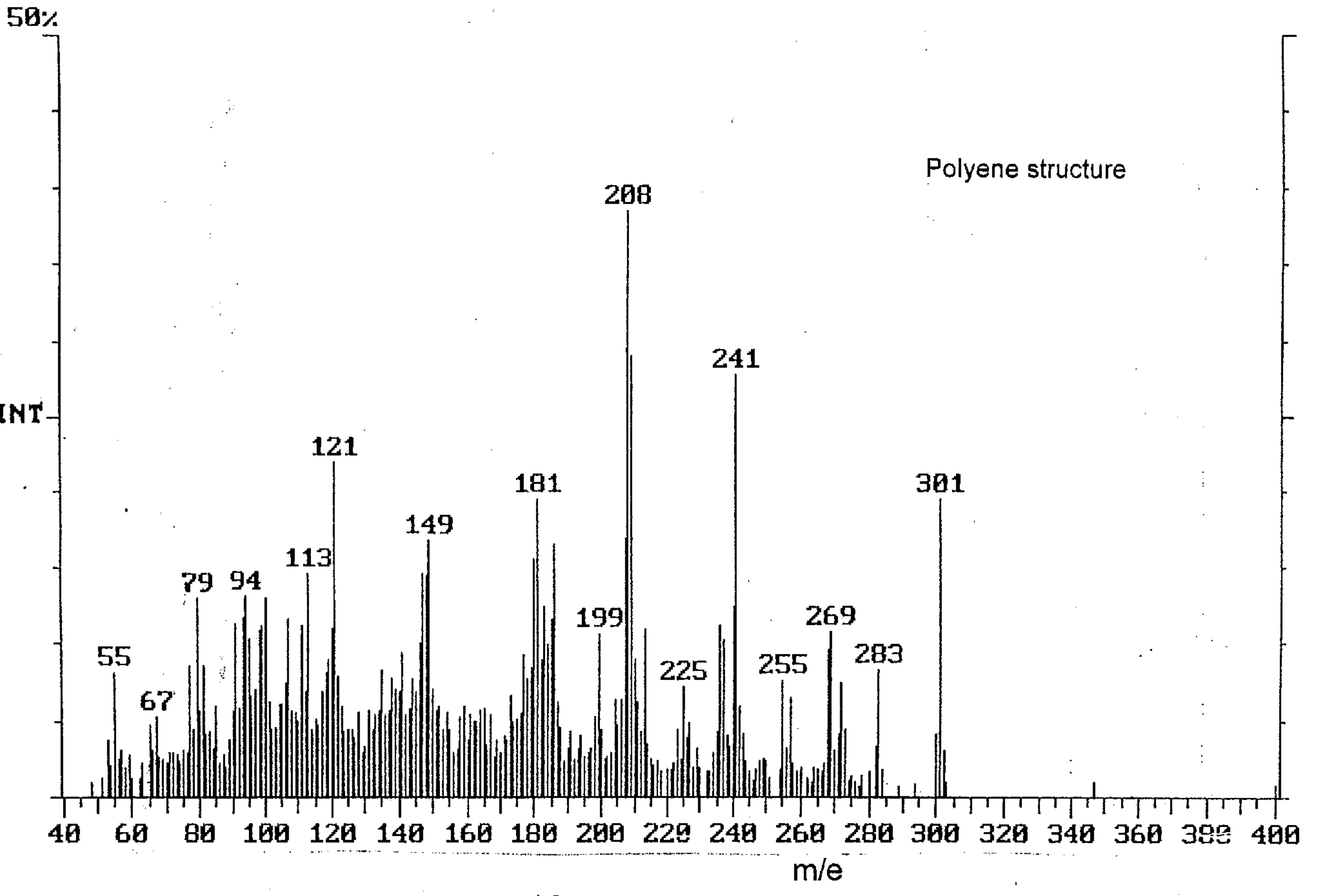


Figure 4.19: Mass spectrum of compound 8.

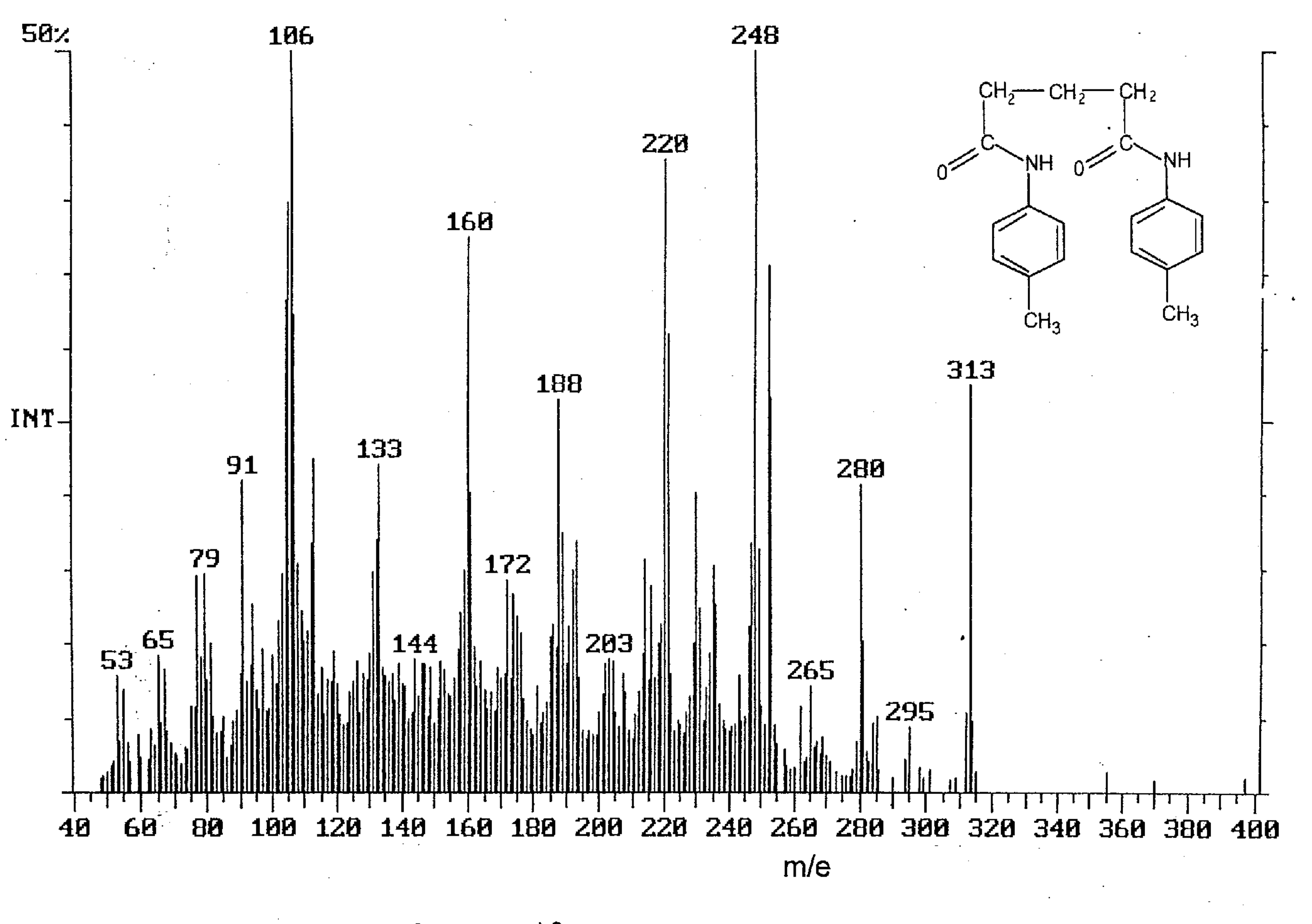


Figure 4.20: Mass spectrum of compound 9.

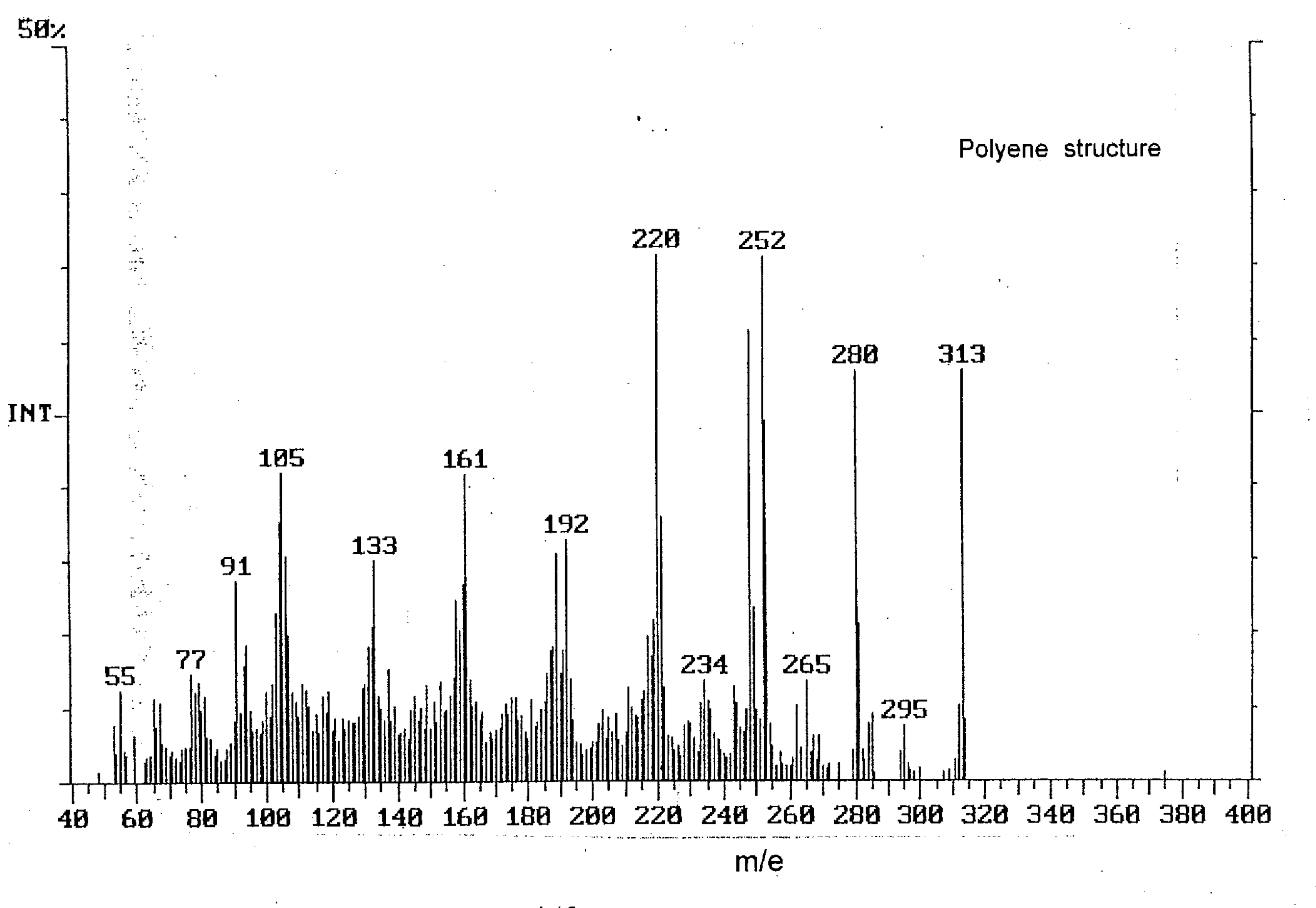


Figure 4.21: Mass spectrum of compound 10.

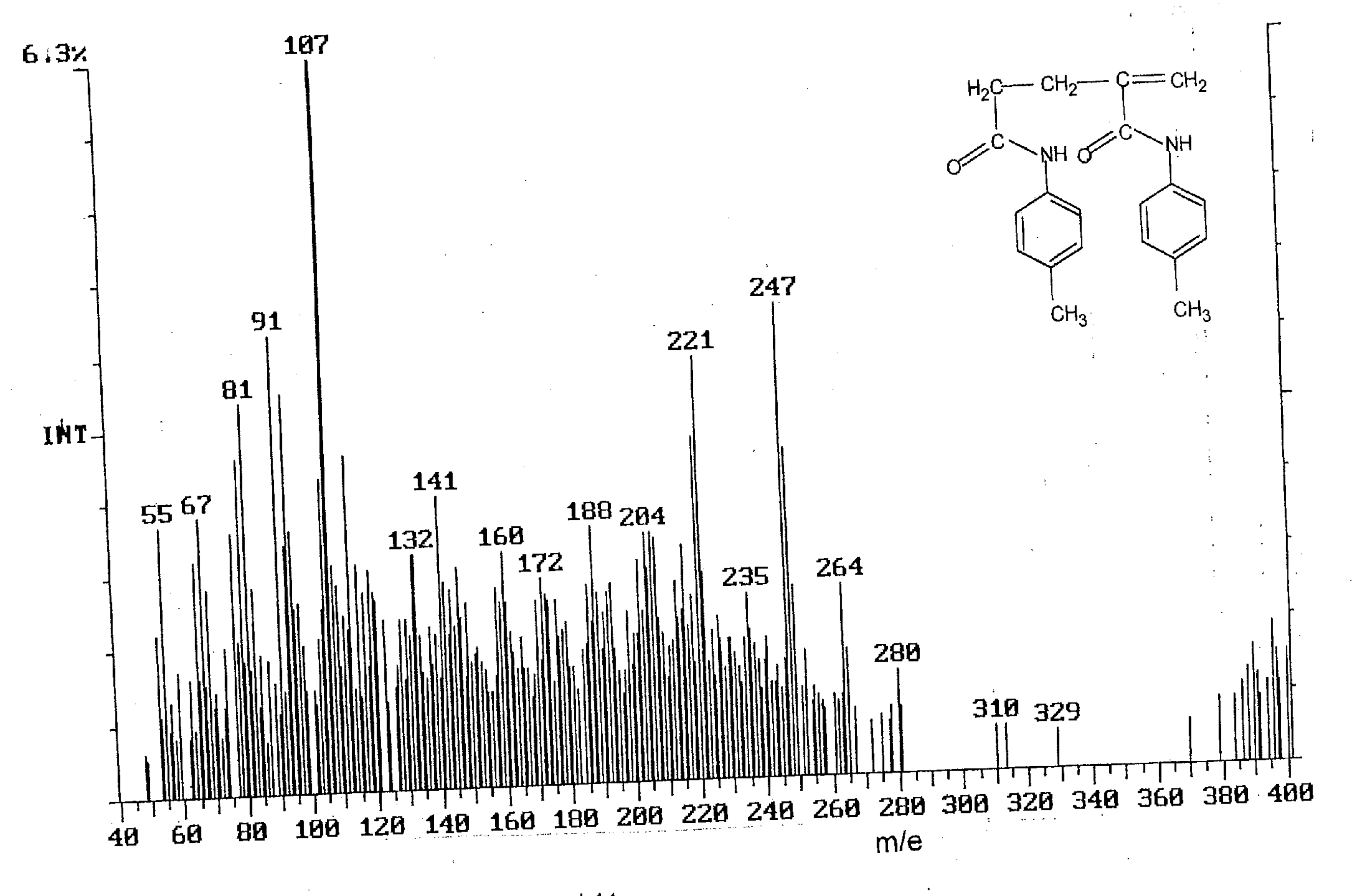


Figure 4.22: Mass spectrum of compound 11.

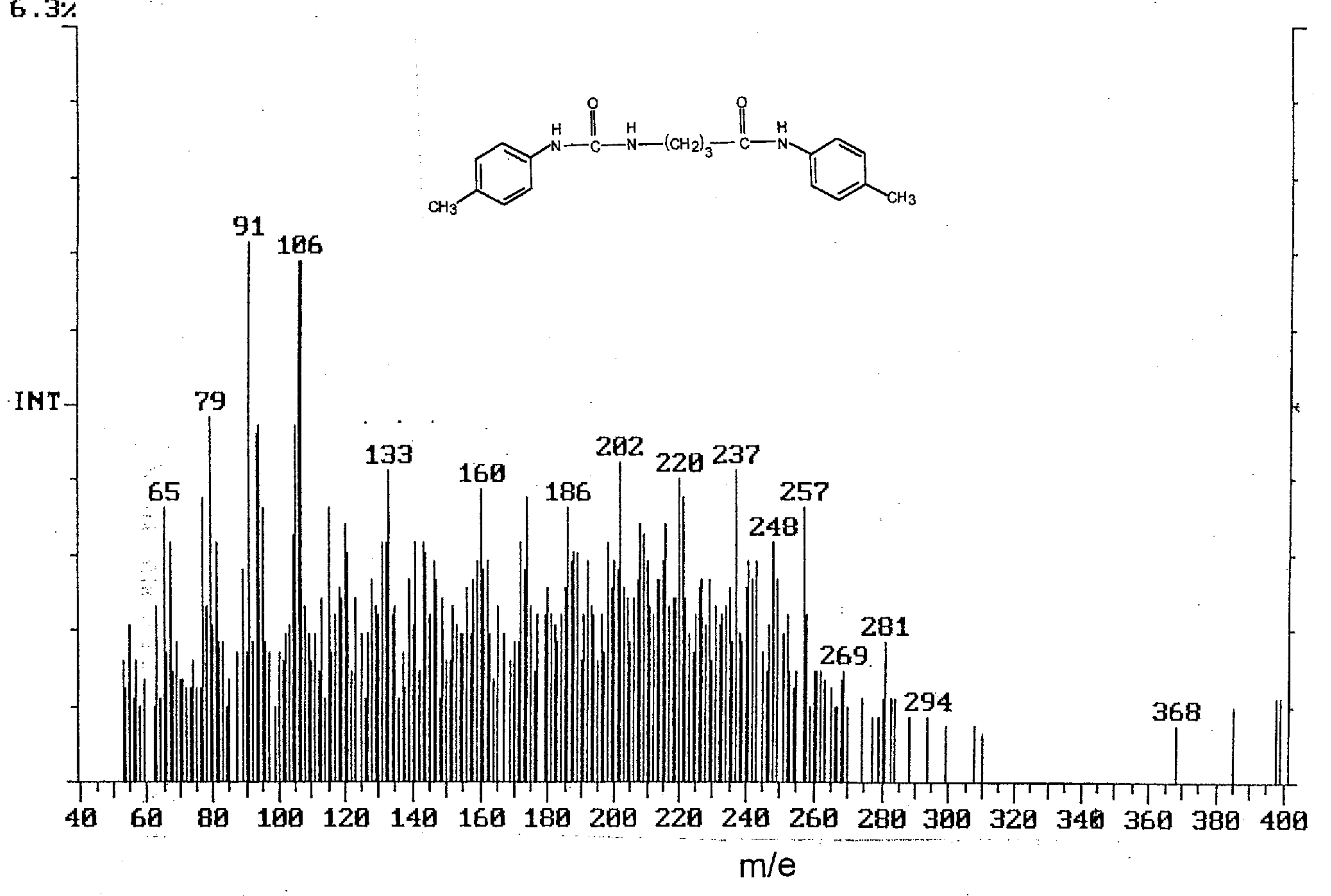


Figure 4.23: Mass spectrum of compound 12.

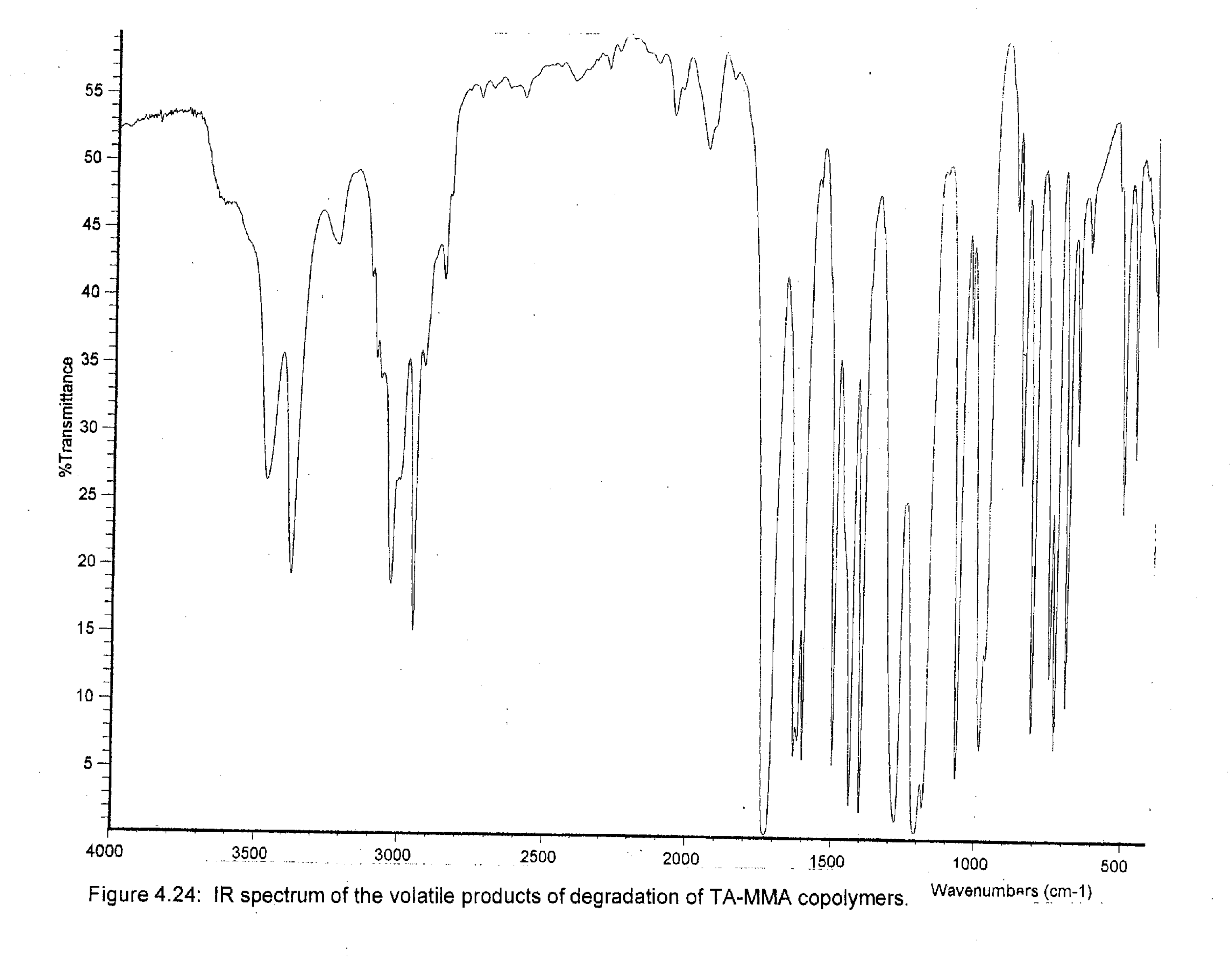


Figure 4.24: IR spectrum of the volatile products of degradation of TA-MMA copolymers.

CHAPTER 5

POLY(p-TOLYL ACRYLAMIDE) HOMOPOLYMER AND COPOLYMERS OF p-TOLYL ACRYLAMIDE WITH METHYL ACRYLATE

CHAPTER 5

POLY(p-TOLYL ACRYLAMIDE) HOMOPOLYMER AND COPOLYMERS OF p-TOLYL ACRYLAMIDE WITH METHYL ACRYLATE

5.1. Introduction:

Commercial applications of PMMA homopolymer may require improved heat resistance and one route to achieve this is through copolymerization. Copolymers of MMA and methyl acrylate (MA) should be better thermal stability than PMMA homopolymer[110].

In this Chapter, homopolymer of methyl acrylate (PMA) and a range of TA-MA copolymers covering the entire composition range between PTA and PMA homopolymers have been prepared and the reactivity ratios of copolymerization were calculated. The thermal stabilities and degradation behaviours of the homopolymers and copolymers were investigated. The activation energies of the decomposition of the copolymers were determined using Arrhenius relationship.

5.2. Characterization of PMA homopolymer and TA-MA copolymers:

PMA homopolymer was prepared by free radical initiation using AIBN as initiation and DMF (50/50 v/v) as solvent. The polymerization was carried to about 10% conversion. PMA was precipitated in distilled water, and dried under vacuum. The IR spectrum of PMA homopolymer as shown in Figure 5.1 exhibits a strong characteristic band at 1730 cm^{-1} attributed to the asymmetric stretching vibration of the carbonyl group of PMA homopolymer.

Copolymers of TA-MA were prepared using AIBN as initiator and DMF (50/50 v/v) as solvent. Polymerization were carried out to about 5% conversion. The copolymers were precipitated by pouring into a large excess of distilled water and dried in a vacuum oven at $40^{0}C$. The IR spectrum of TA-MA copolymers (Figure 5.2) shows two medium broad bands at 3280 and 3450 cm^{-1} assigned to symmetric and asymmetric stretching vibrations of the amino group. The bands at 1680 and 1730 cm^{-1} are assigned to antisymmetric stretching vibration of the amidic carbonyl group of TA and carbonyl group of MA in the copolymers, respectively[147]. The bands at 1600, 1545 and 1440 cm^{-1} are due to ν(C-H), ν (C=C) and ν (C-C) bonds[148], respectively.

5.3. Determination of reactivity ratios of TA-MA copolymers:

Five different copolymers of TA-MA with 45, 27, 19, 13 and 11 mole % of TA units covering the entire composition range between PTA and PMA homopolymers were prepared, so the reactivity ratios might be determined using ^{1}H-NMR method as discussed in the previous Chapters. Figure 5.3 shows the ^{1}H-NMR spectrum of TA-MA copolymers. The bands at δ 1.65, 2.26 and 2.78-2.86 ppm are due to $-CH_3$, CH_2, CH protons of TA and MA in the copolymers[149]. The band at δ 7.79 ppm is due to the amino group which was disappeared on addition of D_2O. Peak A is a composite peak at δ 6.88-7.22 ppm due to two protons in the ortho-position and two protons in the meta-position of the benzene ring of TA units in the copolymers. Peak B at δ 3.52 ppm is due to $-OCH_3$ protons of MA units in the copolymers. Dividing peak A by four and peak B by three, the monomer composition of the copolymer can be calculated. By knowing the number of moles of the monomer mixture and the molar ratio of the copolymer, reactivity ratios can be calculated by applying the following equation[141].

$$\frac{f_1(1-2F_1)}{(1-f_1)F_1} = \frac{f_1^{\,2}(F_1-1)}{(1-f_1)^2 F_1} r_1 + r_2$$

Where $F_1 = \frac{M_1/M_2}{M_1/M_2 + 1}$ is the mole fraction of TA (M_1) in copolymer, $f_1 = \frac{n_1}{n_1 + n_2}$ is

The mole fraction of M_1 in feed and r_1 and r_2 are the reactivity ratios of TA and

MA, respectively. Figure 5.4 is a plot of $\frac{f_1^2 (F_1-1)}{(1-f_1)^2 F_1}$ versus $\frac{f_1 (1-2F_1)}{(1-f_1)\ F_1}$ and

Figure 5.5 is a plot of $\frac{f_2^2 (F_2-1)}{(1-f_2)^2 F_2}$ versus $\frac{f_2(1-2F_2)}{(1-f_2)\ F_2}$ where $F_2 = \frac{M_2/M_1}{M_2/M_1 + 1}$

is the mole fraction of MA(M_2) in copolymer and $f_2 = \frac{n_2}{n_1 + n_2}$ is the mole fraction of M_2 in feed. From the slopes and intercepts in Figures 5.4 and 5.5, reactivity ratio values for TA-MA copolymers are r_1 (TA) = 0.58 ± 0.1 and r_2 (MA) = 1.52 ± 0.1.

5.4. Thermal methods of analysis:

5.4.1. Thermogravimetry (TG):

TG curves of PTA and PMA homopolymers and TA-MA copolymers are shown in Figure 5.6. PTA homopolymer degrades in two stages as described in chapter 4. The degradation starts at ~ 330°C for PMA homopolymer showing one decomposition stage with weight loss of ~ 90 %. This is similar to the results obtained by Diab[150] in the thermal degradation of poly(vinyl bromide) and blends of poly(vinyl bromide) with poly(methyl acrylate). There are two TG degradation stages for all the TA-MA copolymers. The degradation temperatures started at ~ 200, 225, 255, 275 and 285°C for the copolymers 45, 27, 19, 13 and 11 mole % TA units, respectively. Table 5.1 represents the weight loss percentages and the maximum rate of weight loss shown by the

derivative TG apparatus. Again, TG curves of the copolymers reveal that the stability is intermediate between PTA and PMA homopolymers.

The initial stages of degradation of the homopolymers and copolymers were studied to give a clear picture of relative stability for the entire composition range. The smooth change in stability with composition is well demonstrated in Figure 5.7, in which the weight loss percentage at 360^0C in the programmed degradation using the data in Figure 5.6 is plotted against composition. The most clearly result is the increase of the thermal stability of PTA homopolymer and TA-MA copolymers towards PMA homopolymer.

The effective activation energies for the thermal degradation of PTA and PMA homopolymers and TA-MA copolymers were determined from the temperature dependence of the chain rupture rate. The rate constant of the thermal degradation was plotted according to the Arrhenius relationship (Figure 5.8). Table 5.2 lists the activation energies of the homopolymers and copolymers, from which the values of activation energy of the copolymers increasing from 113.3 to 138.5 KJ/mol were obtained as the MA concentration in the copolymer increases. It is clear that the rate of activation energies are in the same order as the stabilities.

5.4.2. Thermal degradation of PMA homopolymer and TA-MA copolymers:

The thermal degradation of PMA homopolymer was first studied by Straus and Madorsky[151], who found that the main product of degradation (73% by weight) was a low polymer fraction with an average molecular weight of 633. Other volatile products identified were methanol (15%), carbon dioxide (7.5%), methyl acrylate (0.7%), methyl methacrylate (0.1%) and C_4-C_6 oxygenated compounds (3.9%). Straus and Madorsky concluded that because little monomer is formed, the reaction mechanism does not involve free radicals, but may be explained by a disproportionation process:

Cameron and Kane[152,153] concluded that .their results supported Madorsky's view of a random chain scission process but did not exclude the possibility of weak links. They also suggested that the low polymer fraction of the products of degradation may be explained by random homolytic back-bone scission followed by a chain of free radical transfer reactions. The following mechanism has been suggested for the formation of carbon dioxide from the degradation of PMA:

Methanol could be formed as follows:

$$H^{\cdot} + {}^{\cdot}OCH_3 \longrightarrow CH_3OH$$

Figure 5.9 shows the IR spectrum of the volatile degradation products of TA-MA copolymers. The bands at 3190, 3360 and 3430 cm^{-1} are due to symmetric and asymmetric stretching vibrations of p-toludine. The bands at 1490 and 2150 cm^{-1} attributed to toluene and ammonia, respectively[142]. The characteristic band at 1730 cm^{-1} indicate the presence of MA and MMA monomers among the products of the thermal degradation TA-MA copolymers. The degradation liquid fractions were injected into the GC-MS apparatus. Figure 5.10 shows the GC chromatogram of the liquid products of degradation of TA-MA copolymers. Table 5.3 lists the results of degradation products which were identified by mass spectroscopy. Again the small peaks were ignored due to the lack of reference materials or the uncleared mass spectra. Similar pattern of degradation products as in the PTA homopolymer beside peaks due to MA fragments as shown in Figures 5.11, 5.12 and 5.13. There is no interaction between the two types of monomer units in the copolymer chain. The mechanism of degradation of TA-MA copolymers is characterized by free

radical formation followed by random scission or combination of these radicals as in PTA and PMA homopolymers and by a disproportionation mechanism as PMA homopolymers.

Table 5.1: Weight loss percentage of PTA and PMA homopolymers and TA-MA copolymers

Polymer Mole%TA	Volatilization temperature, °C	First stage		Second stage		Remaining Wt.% after 500°C
		T_{max}, °C	Wt.loss,%	T_{max}, °C	Wt.loss,%	
PTA	112	250	47	370	44	9
45	200	260	18	390	74	8
27	225	270	13	395	79	8
19	255	277	8	400	84	8
13	275	289	6	405	85	9
11	285	300	5	415	87	8
PMA	350	420	90	-	-	10

Table 5.2: Activation energies of the thermal degradation of PTA and PMA homopolymers and TA-PMA copolymers

Polymer mole % TA	Activation energy(Ea) KJ /mol
PTA	43.6
45	113.3
27	121.9
19	127.9
13	130.6
11	138.5
PMA	145.2

Table 5.3: GC-MS data of the liquid fraction of the thermal degradation of TA-MA copolymers.

Compound No.	Retention Time, min.	Major MS fragments	Suggested Structure (Most probable)
1	8.44	174,160,141,129,105, 75, 61,48	MA fragment
2	10.73	As in compound 1 in Figure 4.12	$CH_2=CH-C(=O)-NH-C_6H_4-CH_3$
3	11.53	As in compound 2 in Figure 4.13	$H_3C-C_6H_4-NH-NH-C_6H_4-CH_3$

Cont'd: Table 5.3: GC-MS data of the liquid fraction of the thermal degradation of TA-MA copolymers.

Compound No.	Retention Time, min.	Major MS fragments	Suggested Structure (Most probable)
4	12.11	As in compound 3 in Figure 4.14	
5	13.93	As in compound 4 in Figure 4.15	
6	14.58	As in compound 5 in Figure 4.16	

Cont'd: Table 5.3: GC-MS data of the liquid fraction of the thermal degradation of TA-MA copolymers.

Compound No.	Retention Time, min	Major MS fragments	Suggested Structure (Most probable)
7	15.40	As in compound 6 in Figure 4.17	
8	15.73	As in compound 7 in Figure 4.18	
9	17.96	As in compound 8 in Figure 4.19	Polyene structure.
10	18.09	327,301,283,269,257,236,225,204, 183,141,129,101,48	MA fragments

Cont'd: Table 5.3: GC-MS data of the liquid fraction of the thermal degradation of TA-MA copolymers.

Compound No.	Retention Time, min	Major MS fragments	Suggested Structure (Most probable)
11	18.30	As in compound 9 in Figure 4.19	CH_2—CH_2—CH_2; C=O; NH; NH; CH_3; CH_3
12	18.41	As in compound 10 in Figure 4.20	Polyene structure
13	18.73	As in compound 11 in Figure 4.21	H_2C—CH_2—C=CH_2; C=O; NH; NH; CH_3; CH_3

Cont'd: Table 5.3: GC-MS data of the liquid fraction of the thermal degradation of TA-MA copolymers.

Compound No.	Retention Time, min	Major MS fragments	Suggested Structure (Most probable)
14	19.18	As in compound 12 in Figure 4.22	CH_3, $\overset{H}{N}-\overset{O}{\overset{\parallel}{C}}-\overset{H}{N}-(CH_2)_3-\overset{O}{\overset{\parallel}{C}}-\overset{H}{N}$, CH_3
15	23.56	413,399,387,367,339,307,275,247,227,199,172,141,61	MA fragment

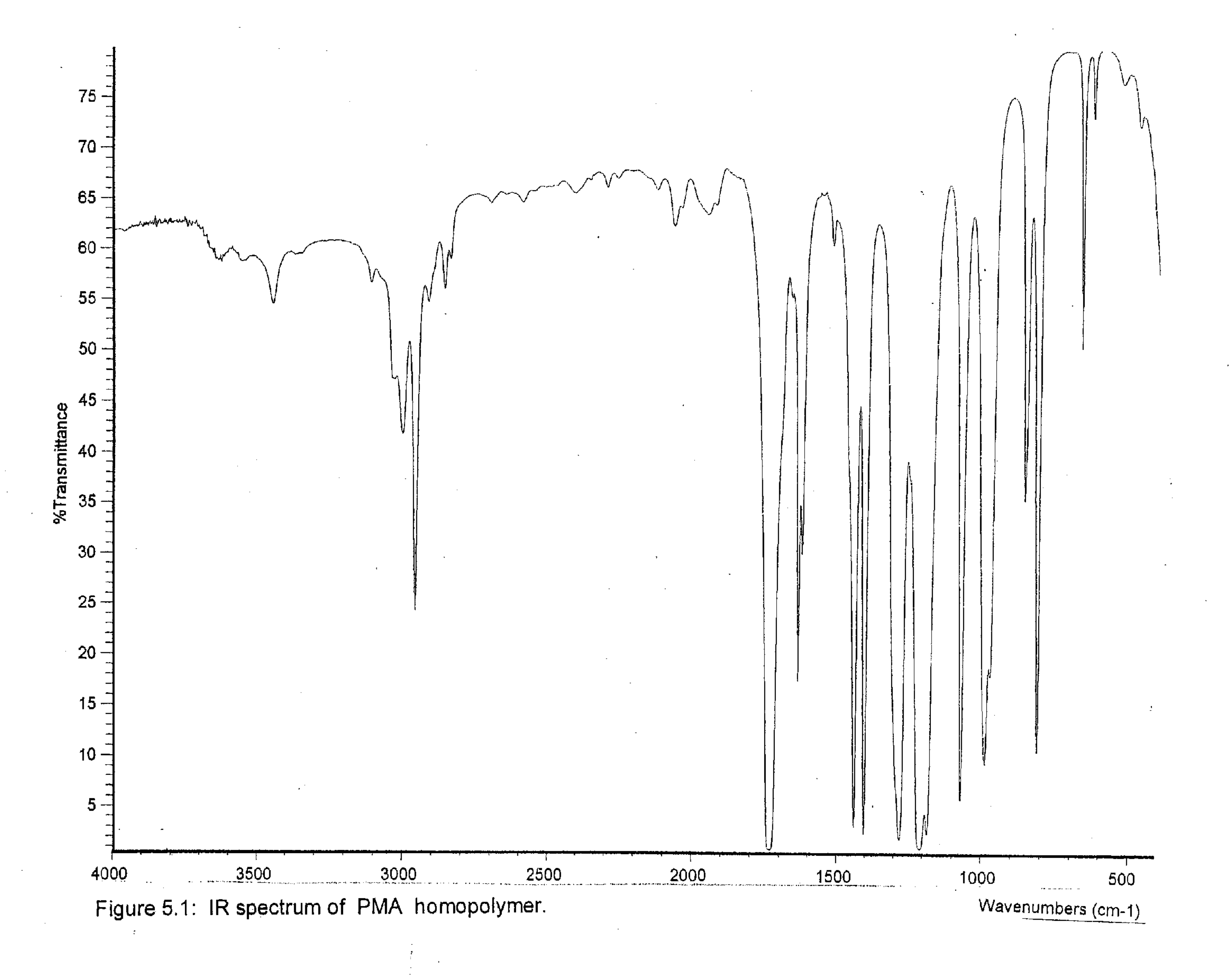


Figure 5.1: IR spectrum of PMA homopolymer.

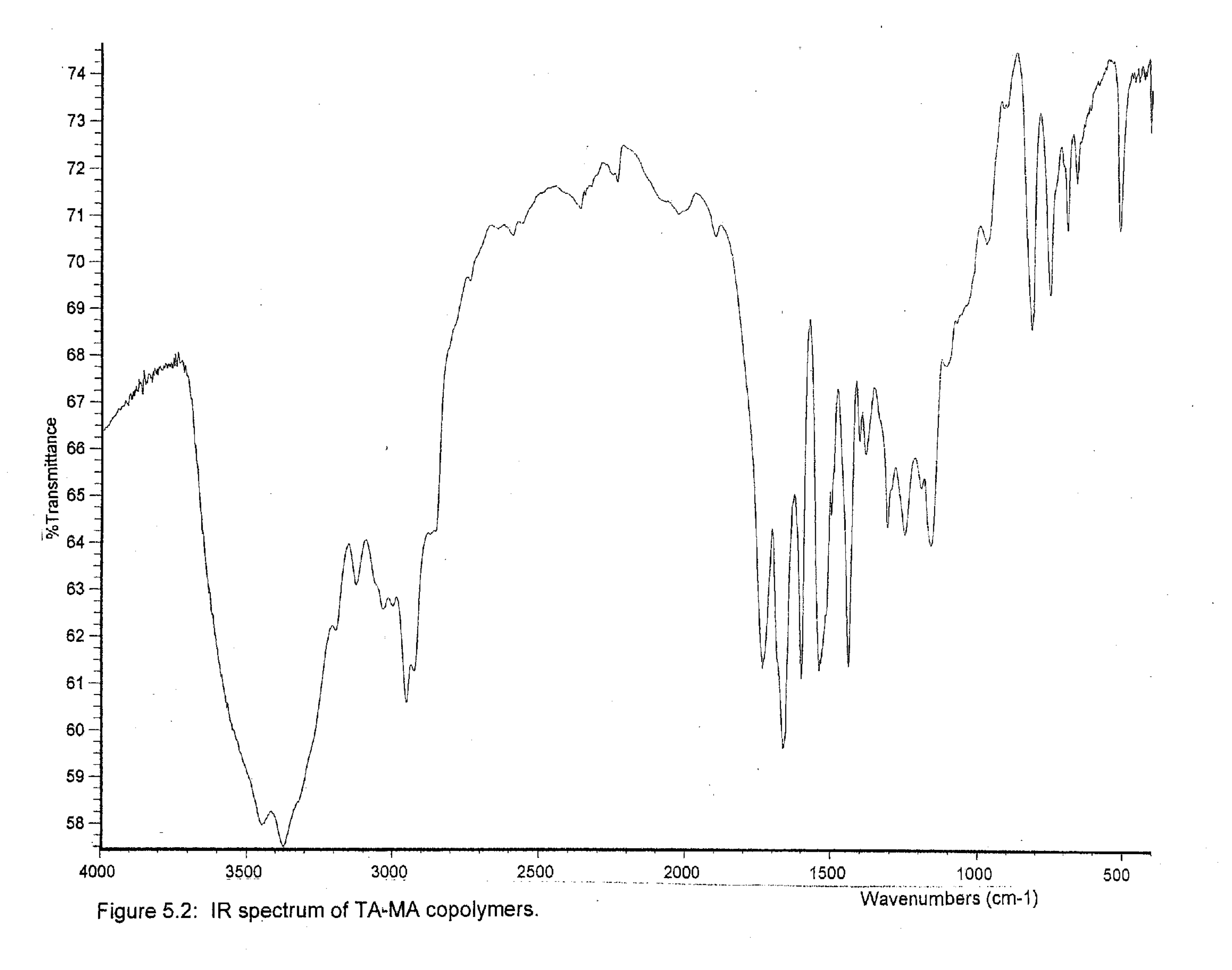


Figure 5.2: IR spectrum of TA-MA copolymers.

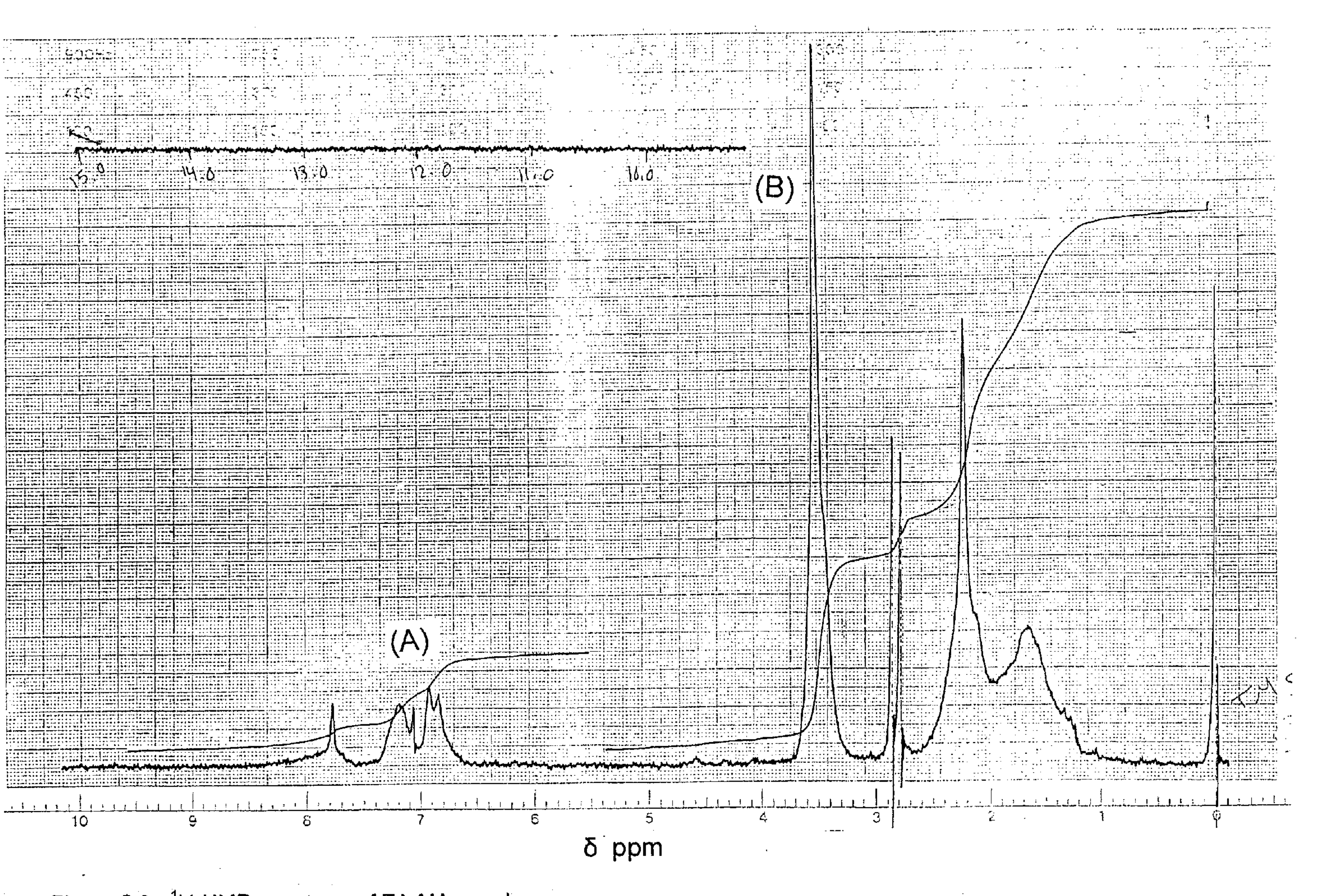


Figure 5.3: ^{1}H-NMR spectrum of TA-MA copolymer.

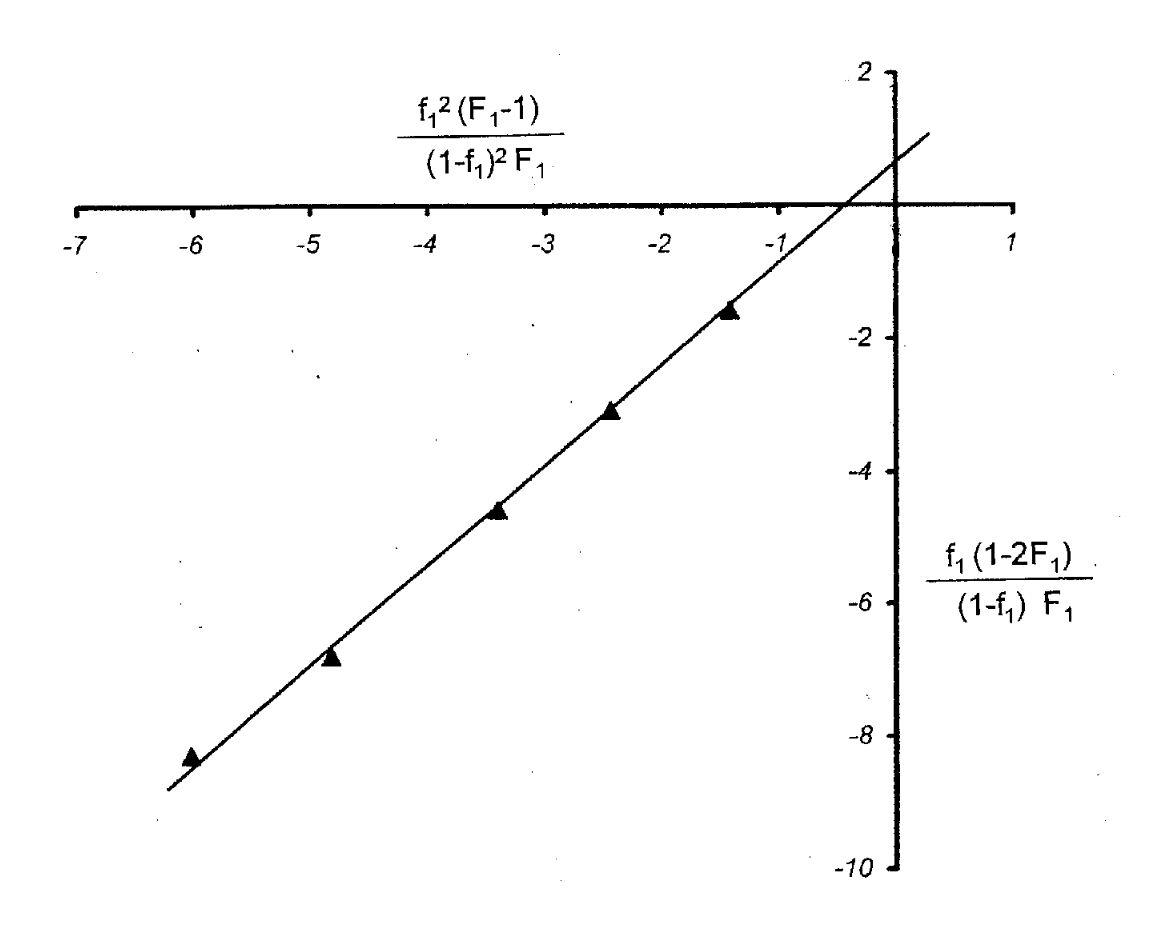


Figure 5.4: Graph of $\frac{f_1^2 (F_1-1)}{(1-f_1)^2 F_1}$ versus $\frac{f_1 (1-2F_1)}{(1-f_1)\ F_1}$ for TA-MA copolymers.

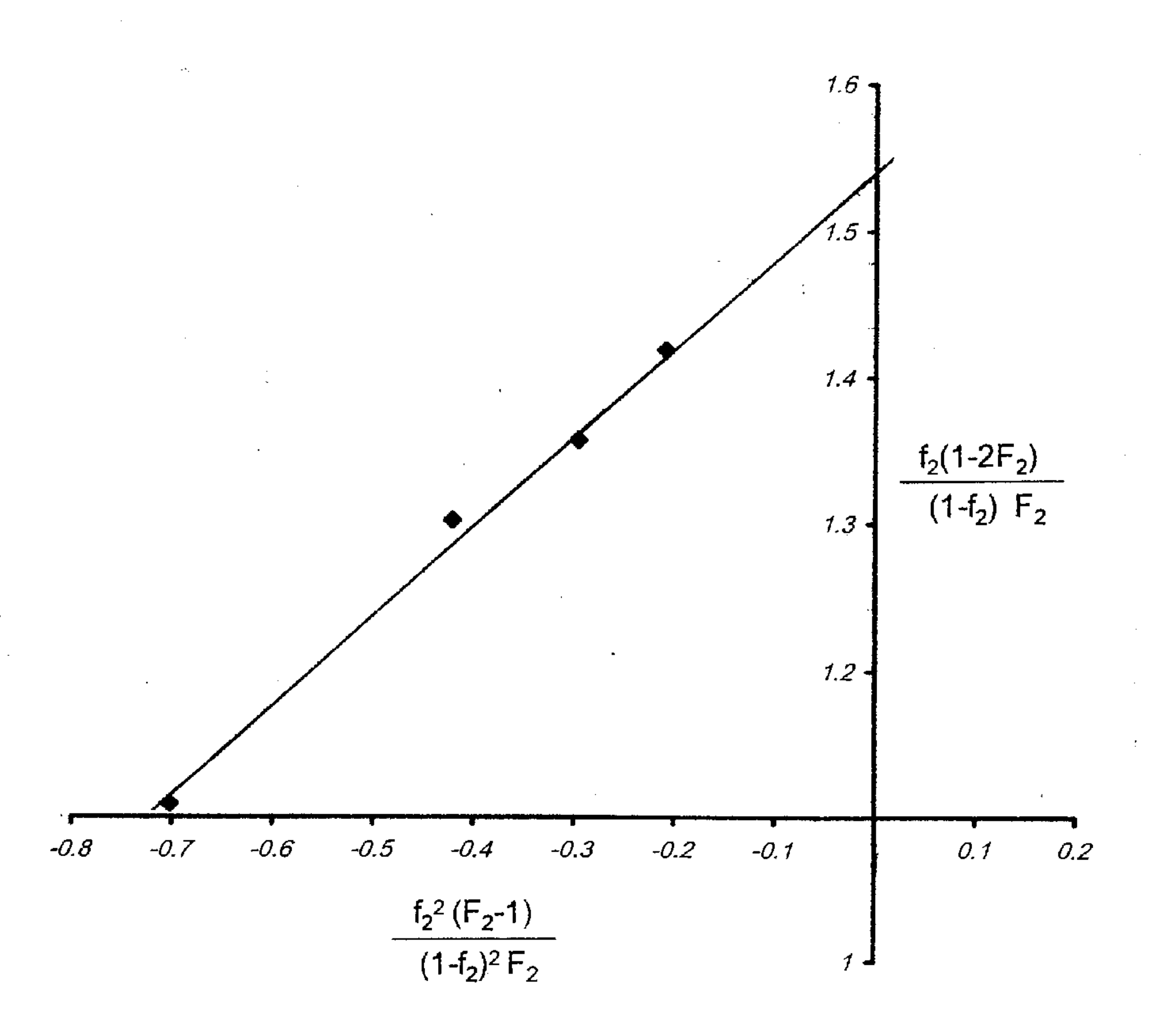


Figure 5.5: Graph of $\frac{f_2^2\,(F_2-1)}{(1-f_2)^2\,F_2}$ versus $\frac{f_2(1-2F_2)}{(1-f_2)\ F_2}$ for TA-MA copolymers.

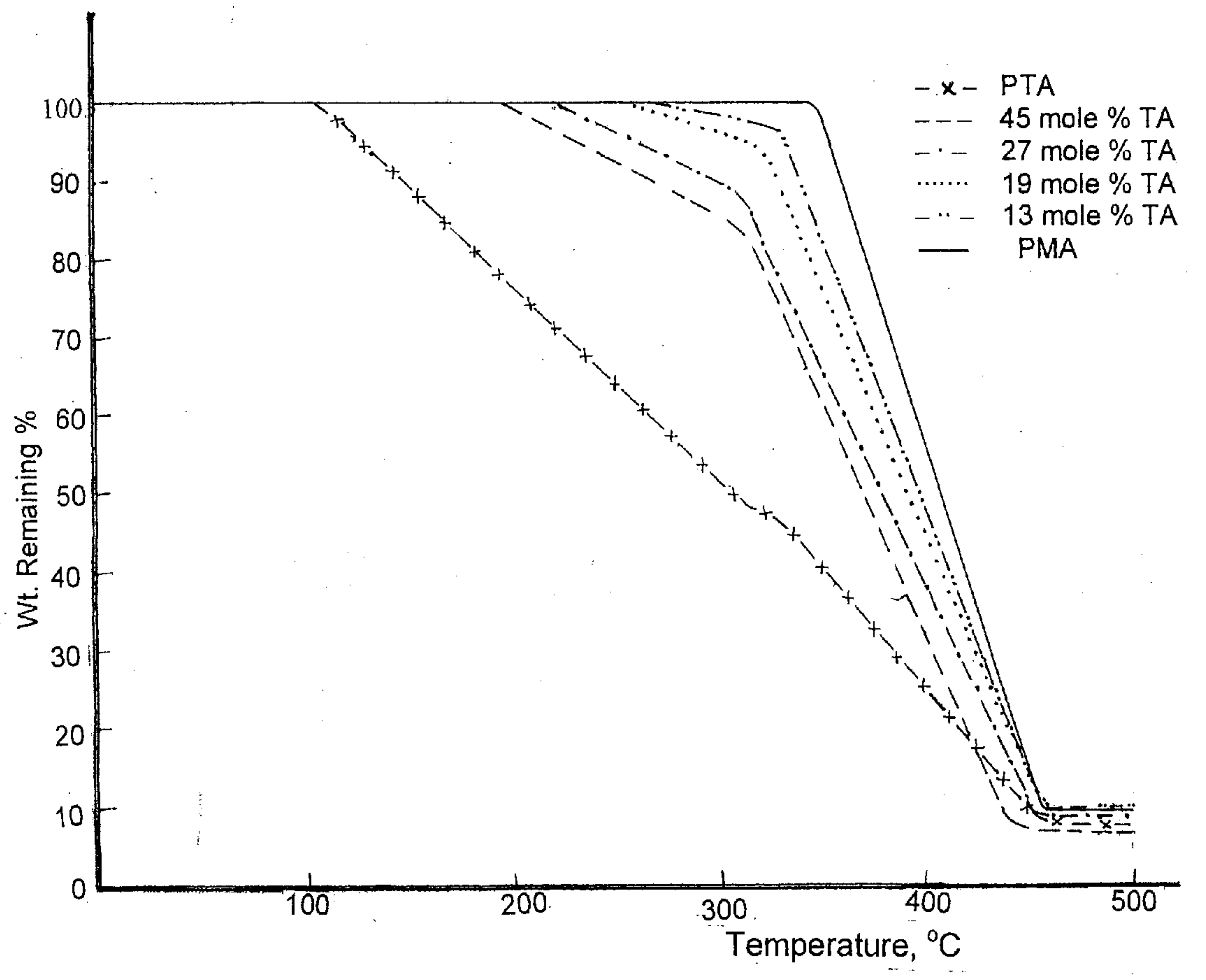


Figure 5.6: TG curves of PTA and PMA homopolymers and TA-MA copolymers.

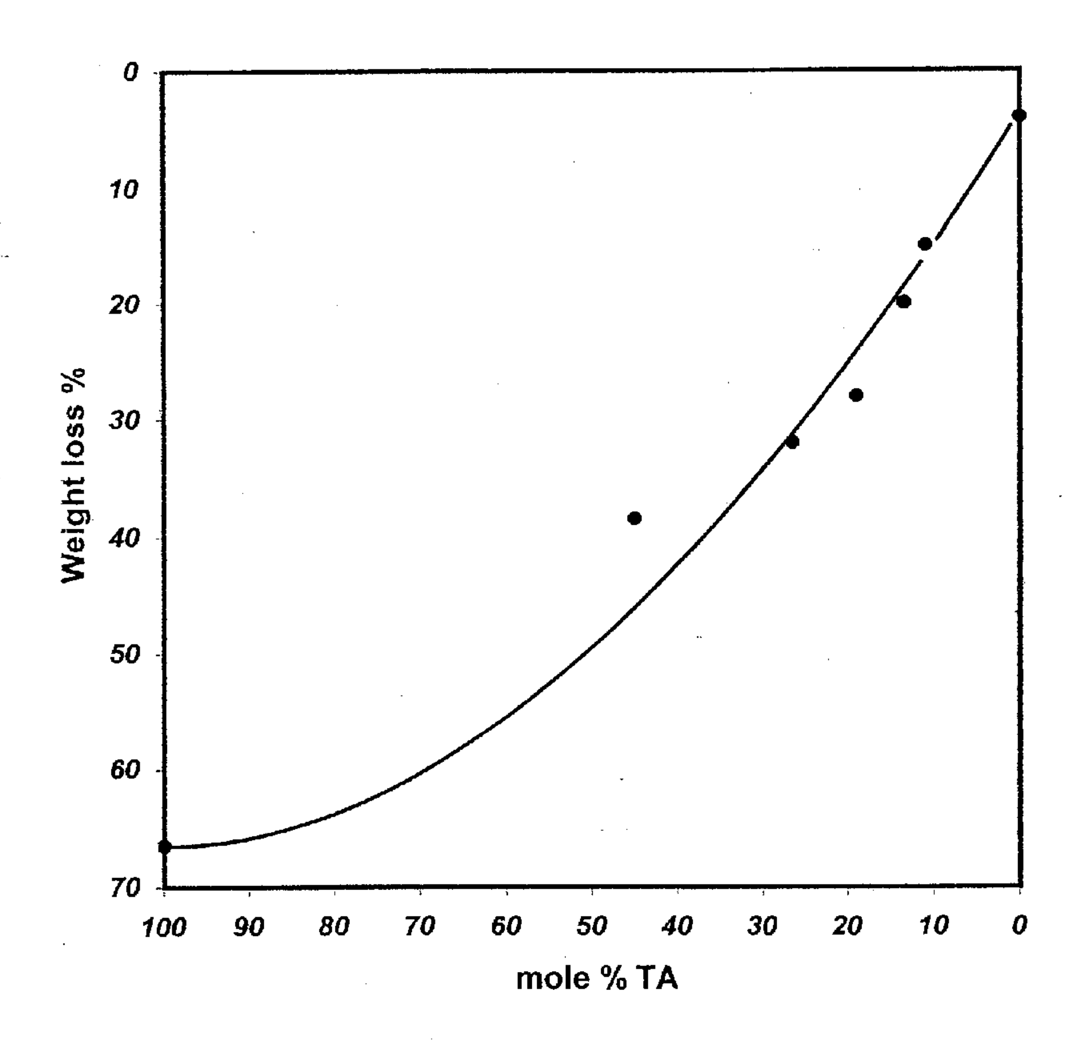


Figure 5.7: Comparison of weight loss percentage at 360 °C for TA-MA copolymers at different compositions.

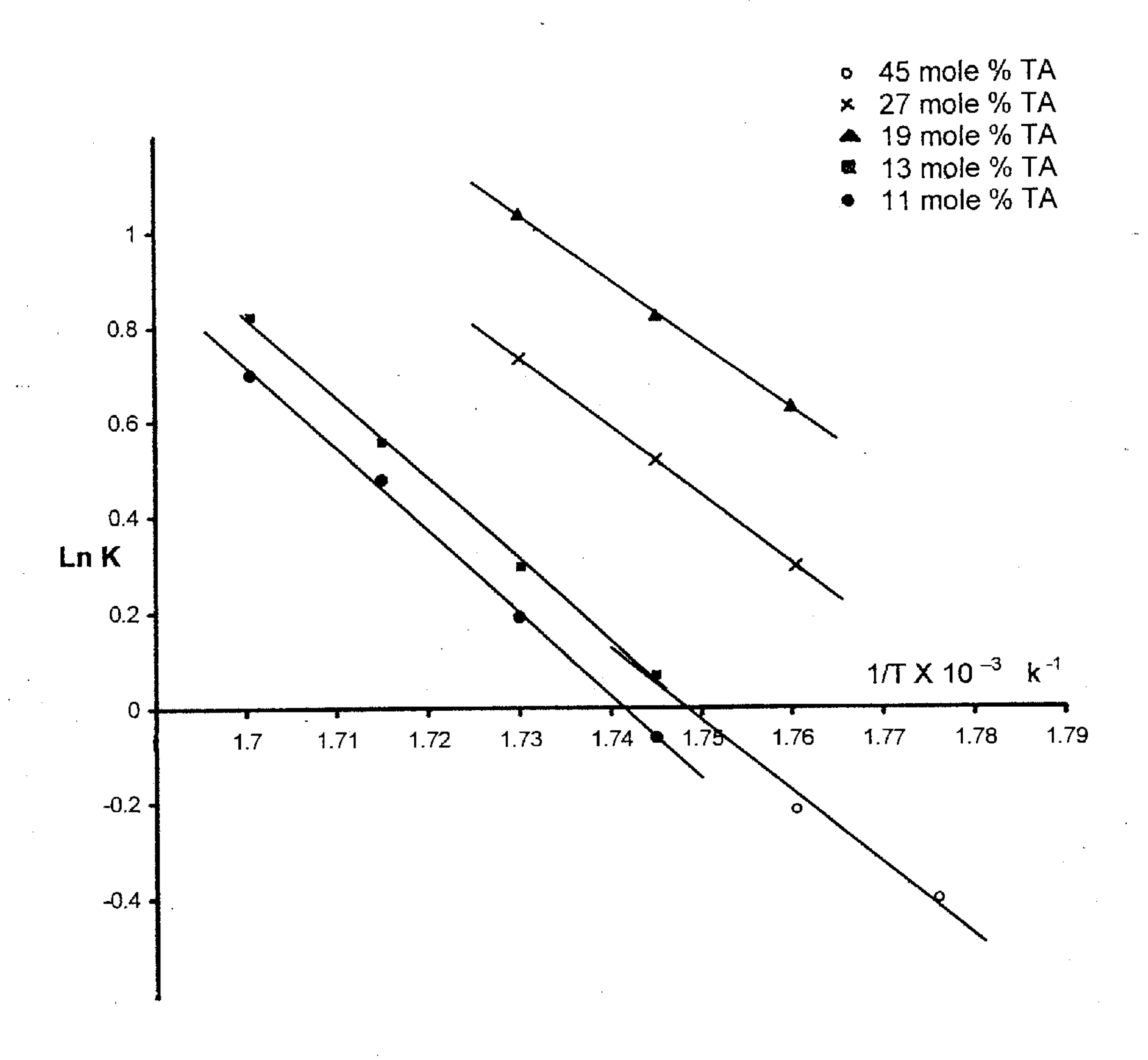


Figure 5.8: Arrhenius plots of the rate constants of degradation of TA-MA copolymers.

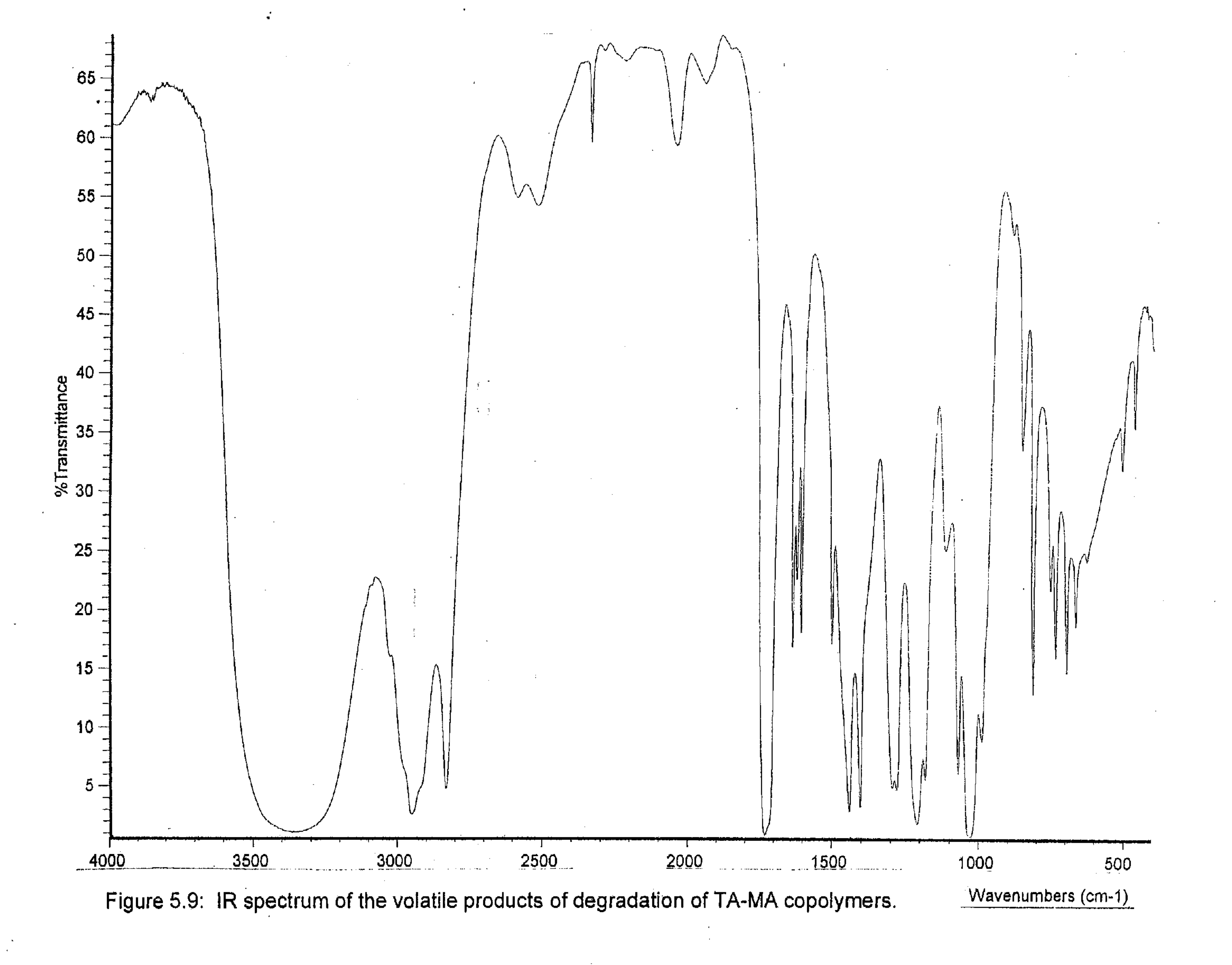


Figure 5.9: IR spectrum of the volatile products of degradation of TA-MA copolymers.

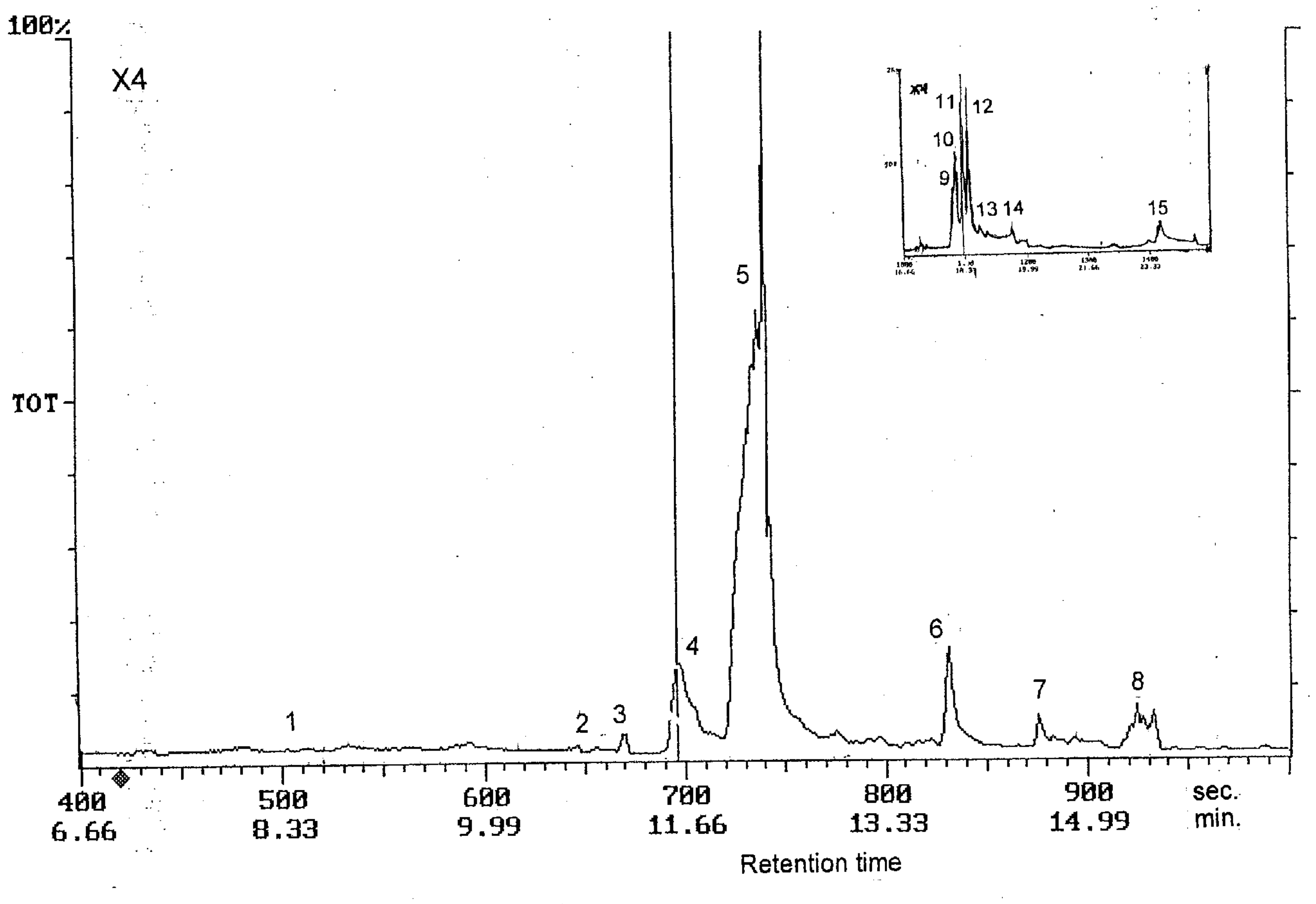


Figure 5.10: GC curve of the liquid fraction of thermal degradation of TA-MA copolymers.

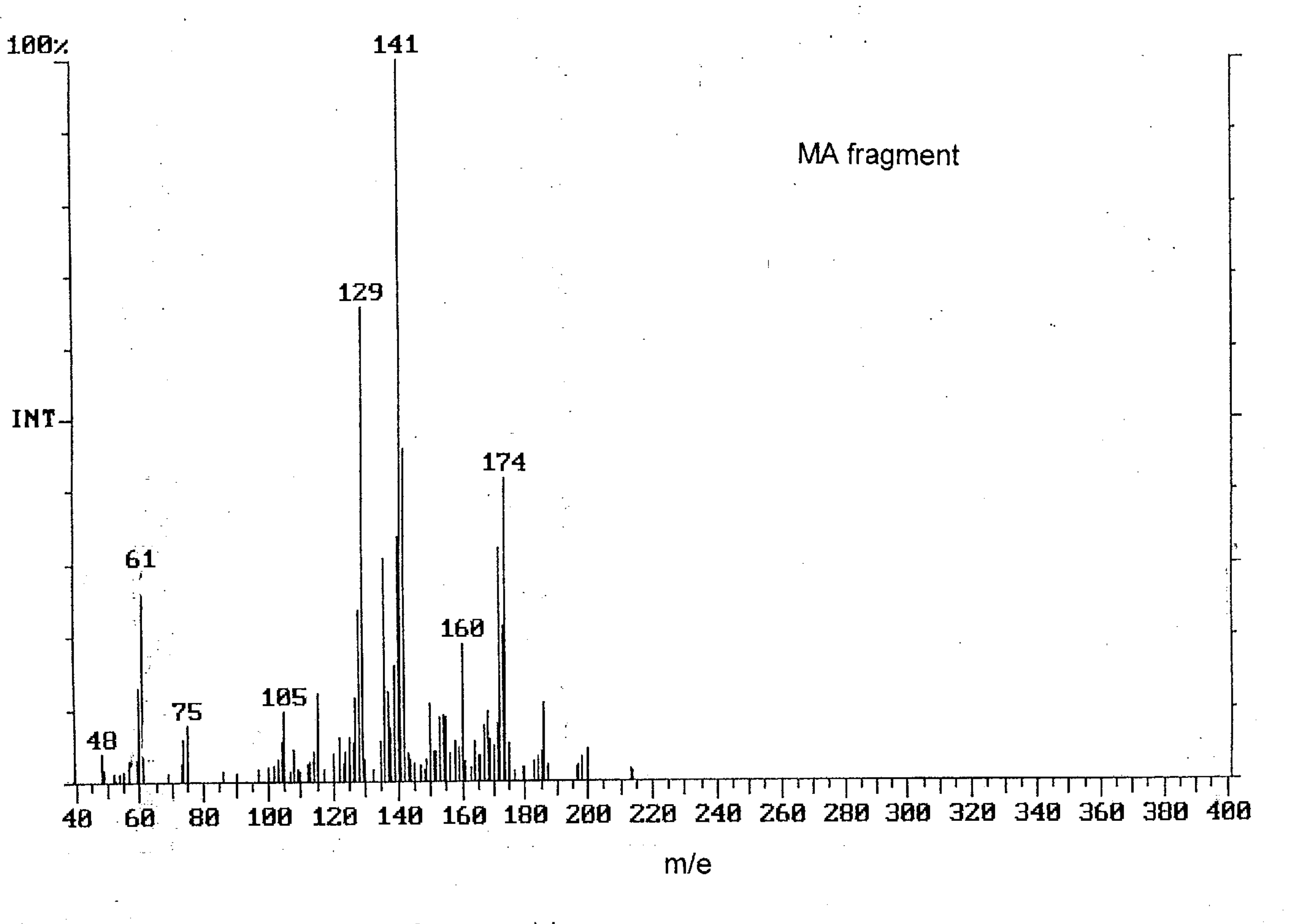


Figure 5.11: Mass spectrum of compound 1.

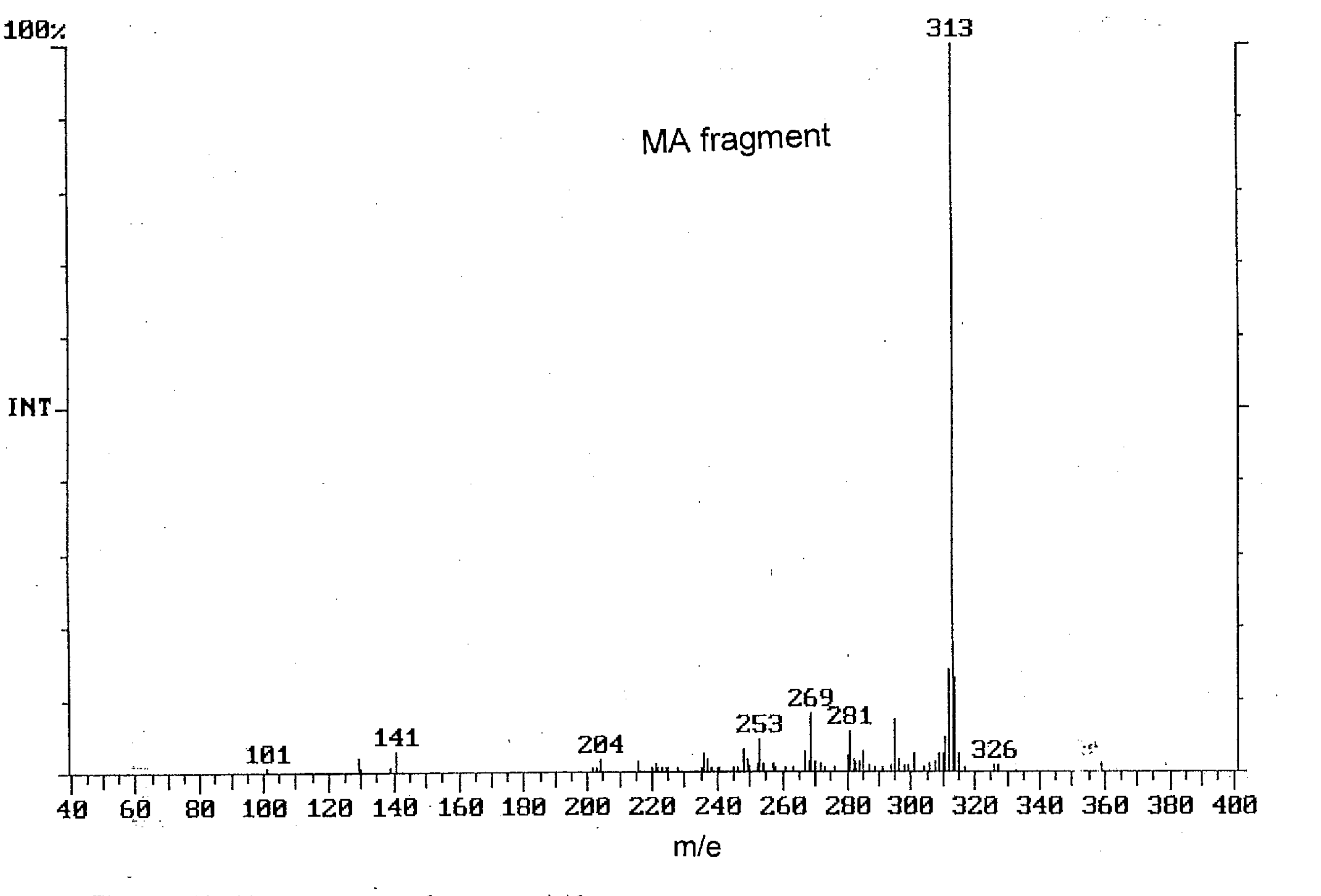


Figure 5.12: Mass spectrum of compound 10.

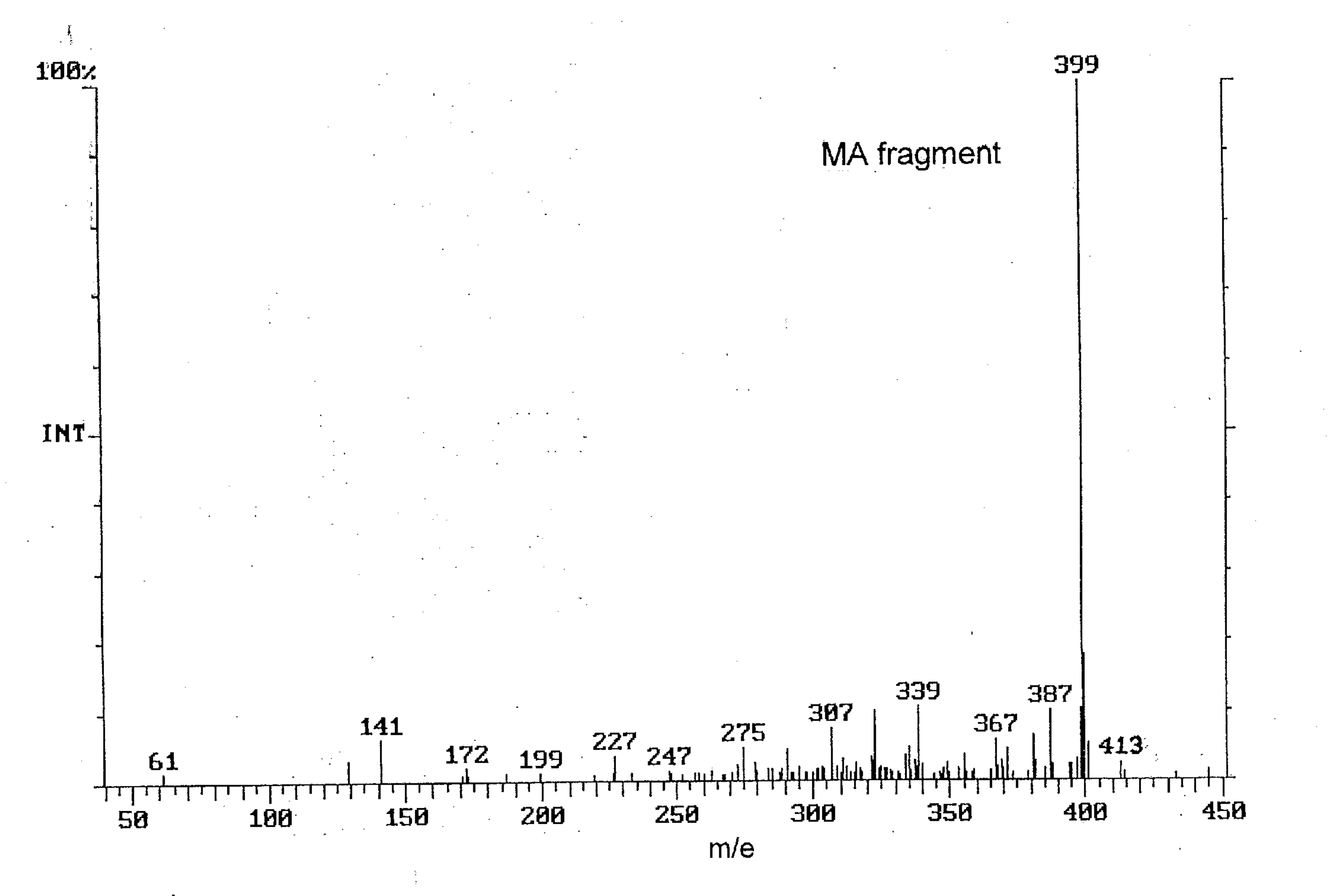


Figure 5.13: Mass spectrum of compound 15.

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SUMMARY

SUMMARY

It is well known that the thermal stability of polymers has been given a great deal of attention for many years. One route to achieve thermally stable polymers is through copolymerization of the primary monomer with traces of a comonomer.

The present work involves preparation of poly(phenyl acrylamide) (PPA), poly(p-tolyl acrylamide) (PTA) homopolymers and copolymers of phenyl acrylamide (PA) and p-tolyl acrylamide (TA) with methyl methacrylate (MMA) and methyl acrylate (MA). The thermal stabilities of the homopolymers and copolymers were investigated. Thermal degradation of the homopolymers and copolymers have been studied in order to determine the nature of the degradation products and the activation energies of degradation were calculated.

Chapter 1 of this five Chapters thesis, includes a literature survey on the mechanisms of stabilization and degradation of polymers.

Chapter 2 discusses the preparation of monomers, homopolymers and copolymers under investigation. Analytical techniques and thermal methods of analysis were provided.

Five different concentrations of copolymer of PA-MMA covering the entire composition range were prepared and characterized in Chapter 3. The reactivity ratios of copolymerization were determined using ^{1}H-NMR method and found to be r_1 (PA) = 0.21± 0.01 and r_2 (MMA) = 2.0± 0.2. Thermogravimetric analysis shows that the stabilities of the copolymer are intermidiate between PPA and PMMA homopolymers. The numerous degradation products of PPA homopolymer indicate that the mechanism of degradation is characterized by the elimination of low-molecular weight radicals.

Combination of these radicals and random scission mechanism along the backbone chain are the main source of the degradation products. The degradation products of PA-MMA copolymers show similar pattern of GC-MS chromatogram as in PPA and PMMA homopolymers suggesting that there is no interaction between the two types of monomers in the degradation of copolymers.

In Chapter 4, PTA and PMMA homopolymers and five different compositions of copolymer of TA-MMA were prepared and characterized by using microanalysis, IR and ^{1}H-NMR spectroscopic techniques. The reactivity ratios of copolymerization were determined and found to be r_1 (TA) = 1.4 ± 0.1 and r_2 (MMA) = 2.8 ± 0.1. TG curves reveal that the stability of the copolymers is intermediate between PTA and PMMA homopolymers. The effective activation energies of the thermal degradation of the homopolymers and copolymers were determined using Arrhenius relationship and found to be increase in the same order as the stabilities. The degradation products of PTA homopolymer were identified by IR spectroscopy and GC-MS techniques. Again, it seems that the thermal break-down occurs mainly in the C-N and carbonyl C-C bonds forming low-molecular weight radicals. The thermal degradation of TA-MMA copolymers indicates that there is no interaction between the comonomers in the degradation of copolymers.

A range of TA-MA copolymers covering the entire composition range between PTA and PMA homopolymers were prepared in Chapter 5. The reactivity ratios of copolymerization were determined using ^{1}H-NMR method and found to be r_1 (TA) = 0.58 ± 0.1 and r_2 (MA) = 1.52 ± 0.1. Thermogravimetric analysis shows that there is an increase of the thermal stability of PTA homopolymer and TA-MA copolymers towards PMA homopolymer. The degradation mechanism of TA-MA copolymers involve disproportionation process and random homolytic backbone scission as in PMA homopolymer and free radical formation as in PTA homopolymer degradation.

The values of the activation energy for the thermal degradation of the copolymers were determined and found to be increasing from 113.3 to 138.5 KJ/mol as the MA concentration of the copolymers increase.

ARABIC SUMMARY